REMOVAL OF NITRIC OXIDE (NO) USING HIGH ENERGY ELECTRON BEAM AND DIELECTRIC BARRIER DISCHARGE

SITI A'IASAH BINTI HASHIM

FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR

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SITI A'IASAH BINTI HASHIM

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Name of Candidate: **SITI A'IASAH BINTI HASHIM**

I/C/Passport No: **620101-05-5092**
Regisration/Matric No.: **SHC070077**
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ABSTRACT

Nitric oxide is a gaseous air pollutant which is a precursor to nitrogen oxides and in the atmosphere it reacts chemically with gaseous hydrocarbons to form other photochemical contaminants such as ozone (O_3), peroxyacetal nitrate (PAN) and other photochemical oxidants. Non thermal plasma methods namely, electron beam and dielectric barrier discharge have been studied as promising methods to control NO/ NO_x. Basically both methods run as plasma oxidation process where excited electrons produce radicals that will oxidize the targeted pollutants. Investigations using the electron beam flue gas treatment indicate that processing temperature, moisture content, beam current and radiation dose are the important parameters in determining the removal efficiency of nitric oxides. Removal efficiency of 90% was obtained by providing absorbed dose of 14 kGy, and by keeping the humidity of the flue gases at the inlet, to about 13% v/v and temperature around 70 °C. Experiments using the DBD reactor were carried out at room temperature using different mixtures of gases. With the right combination of flow rate, discharge voltage, number of DBD cells and connecting configuration, the reactor can remove up to 80% nitric oxide in the reduction mode. Side by side, the two methods have potentials for applications depending on the processing flow rate, safety and technical requirements.

ABSTRAK

Nitrik oksida adalah gas pencemar udara yang merupakan pelopor kepada oksida nitrogen dan dalam atmosfera ia bertindak balas secara kimia dengan gas hidrokarbon untuk membentuk bahan cemar fotokimia lain seperti ozon (O_3), nitrat peroxyacetal (PAN) dan oksida fotokimia lain. Kaedah plasma suhu rendah khususnya alur elektron dan nyahcas dielektrik berhalangan merupakan kaedah yang berpotensi untuk mengawal NO / NO_x. Pada asasnya kedua-dua kaedah ini adalah proses pengoksidaan plasma di mana elektron teruja menghasilkan radikal yang akan mengoksidakan bahan pencemar yang disasarkan. Kajian menggunakan kaedah alur electron menunjukkan bahawa suhu pemprosesan, kandungan kelembapan, arus alur dan dos radiasi adalah parameter penting dalam menentukan kecekapan penyingkiran oksida nitrik. Kecekapan penyingkiran 90% boleh dicapai apabila gas tercemar terdedah pada dos sinaran terserap 14 kGy, disamping menjaga kelembapan gas serombong di bahagian masuk pada tahap kira-kira 13% v/v dan suhu sekitar 70 °C. Ujian menggunakan reaktor DBD yang telah dijalankan pada suhu bilik menggunakan campuran yang berbeza gas. Dengan kombinasi kadar aliran, voltan nyahcas, bilangan sel-sel DBD dan konfigurasi penyambungan, reaktor ini mampu menghapuskan sehingga 80% oksida nitrik dalam mod penurunan (reduction). Kedua-dua kaedah ini mempunyai potensi aplikasi bergantung kepada kadar aliran pemprosesan, keselamatan dan keperluan teknikal tersendiri.

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عائشة

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LIST OF ABBREVIATION

ABBREVIATION	DESCRIPTION
AELB	Atomic Energy Licensing Board
ALURTRON	Electron irradiation facility at Nuclear Malaysia
API	Air Pollution Index
BF	Bag Filter
BNIP	Budker Institute of Nuclear Physic
CC	Combined Cycle
CEM	Continuous emission monitor
CTA	Cellulose triacetate
DBD	Dielectric barrier discharge
DOE	Department of Environment
EB	Electron beam
EBFG	Electron beam flue gas
EBFGT	electron beam flue gas treatment
EBM	Electron beam machine
ELV	Electron beam machine made by BINP
EPA	Environmental Protection Agency
EPS 3000	3MeV electron beam processing system
eV	Electron volt
GHG	Greenhouse gases
Gy	Gray (measure of radiation dose)
HNO_2	Nitrous acid
HNO_3	Nitric acid

ABBREVIATION	DESCRIPTION
HO_2	Hydroperoxyl
HV	High voltage
HVPS	High voltage power supply
IAEA	International Atomic Energy Agency
IAEA TECHDOC	Technical document published by IAEA
ID	Inner diameter
IGCC	Integrated Coal Gas Combined Cycle
IMO	International Marine Organization
INCT	Institute of Nuclear Chemistry and Technology
IPP	Independent Power Provider
MW	Megawatt
NH_3	Ammonia
NH_4NO_3	Ammonium nitrate
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxide (general)
O_3	Ozone
OD	Outer diameter
OH	Hydroxyl
PAH	Polyaromatic hydrocarbon
PAN	Peroxyacetal nitrate
PM^{10}	Particulate matter (of 10 micron size)
ppm	Part per million
PV	Process vessel

ABBREVIATION	DESCRIPTION
SC	Spray cooler
scfh	Standard cubic feet per hour
SCR	Selective Catalytic Reduction
SNCR	Selective Non-Catalytic Reduction
SO_2	Sulfur dioxide
SSDL	Secondary Standard Dosimetry Lab (Nuclear Malaysia)
TNB	Tenaga Nasional Berhad
TR	Test rig
VOC	Volatile organic compounds

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CHAPTER 1

INTRODUCTION

This thesis presents the work carried out to study the potential of removing gaseous nitric oxide in polluted air stream using dielectric barrier discharge which is a form of non-thermal plasma discharge. It also presents work on NO removal using high energy electron beam irradiation. The latter technique is used for large flow of flue gases while the dielectric barrier discharge is more suitable for low gas flow rates. Both methods employed energized electrons as the main ingredient to react with the targeted pollutants.

This chapter describes the general scenario of air pollution globally and later specifically in Malaysia. The growing demand for electricity and fuel for transportation had significantly contributed to the increasing emission load of NO_x. Thus, more studies on removal of NO which is the precursor to NO_x in the atmosphere need to be done. This chapter also outlines several conventional methods of controlling NO_x as comparison to the proposed methods.

1.1 General concerns on air pollution

Air pollution had attracted global attention that treaties were drawn, and legislation was tabled to control further damage to the atmosphere. The Montreal Protocol, for example, had undergone seven revisions, the latest in 1999 in Beijing, to ensure that the ozone layer can be recovered by 2050. The treaty was designed to protect the ozone layer by phasing out the production of numerous substances believed to be responsible for ozone depletion. The Kyoto Protocol, which came about in 1997, was aimed at combating global warming. Countries that had ratified the protocol pledged to commit themselves to the reduction of the four greenhouse gases (GHG), namely carbon dioxide, methane, nitrous oxide and sulfur hexafluoride, and two group of gases (hydrofluorocarbon and perfluorocarbons). In most countries of the world, clean air acts provide guidelines to limit emissions from various sources. In the US, the Clean Air Act requires the Environmental Protection Agency (EPA) to develop and enforce regulations to protect the general public from exposure to the hazardous effect of air pollutions. In Malaysia, the Department of Environment had outlined the emission limit from motor vehicles (except for motorcycles) in the Environmental Quality (Clean Air) Regulations.

Fossil fuel combustion is the most-common contributor to air pollution since it is being used by various industries and the general public, mostly as a source of energy. Emission from fossil fuels contains many types of air pollutants such as carbon dioxides, nitrogen oxides, sulfur dioxides, volatile organic compounds and even heavy metals.

In December 1952, The Great Smog of ’52 or Big Smoke became the biggest air pollution event in London. The cold weather combined with windless condition had collected the airborne pollutants which, at that time came mainly from coal-burning activities, to form a thick layer of smog over the city. It was reported that an estimated 4,000 people had died prematurely, and 100,000 more became ill due to the effect of the smog on human respiratory system. This event had led to several changes in practices and regulation to the United Kingdom, including its Clean Air Act 1956.

Smog is formed when air pollutants react in the atmosphere with sunlight, also known as photochemical smog. The air pollutants can include aldehydes, nitrogen oxides, peroxyacyl nitrates and volatile organic compounds. These chemicals are highly reactive and oxidizing. Photochemical smog can be considered as an adverse effect of modernization and industrialization since it is normally present in modern cities.

1.2 Nitric Oxide

There are seven compounds that make the family of nitrogen oxides (NO_x) namely N_2O, NO, N_2O_2. N_2O_3, NO_2, N_2O_4 and N_2O_5. The US EPA however only regulates NO_2 because it is the most prevalent form of NO_x in the atmosphere that is generated by anthropogenic activities.

Nitric oxide is a gaseous air pollutant which is a precursor to nitrogen oxides that react to form this photochemical smog. It has been known for decades for its adverse effects on human and vegetation. In the atmosphere, NO reacts chemically with gaseous hydrocarbons to form photochemical contaminants such as ozone (O_3), peroxyacetal nitrate (PAN) and other photochemical oxidants. Scientists in the United States had observed the adverse effects of photochemical contaminants to human health especially in the urban areas. Some materials can degrade if exposed to it. It has also been established that nitric oxides (and sulfur dioxides) contributes to the formation of acid deposition (also known as acid rain). Cowling (1982) had indicated that this acid deposition had caused detrimental effects to the ecosystem in the North America and Europe.

At ambient temperature, NO is a colorless, odorless, non-flammable and tasteless gas. However, in the presence of air, it can be oxidized to form nitrogen dioxide (NO_2), a brownish chemically reactive gas. Nitrogen dioxide is also an irritant to human and

corrosive to metals. The US EPA had declared that exposure to NO_2 can affect the sensory perception function for human. Other medical research had indicated that NO_2 can cause pulmonary edema when inhaled at sufficient quantities. Nitrogen oxides (NO_x) usually refer to mixtures of nitric oxide (NO) and nitrogen dioxide (NO_2).

Apart from bringing adverse health effects, NO (and SO_2) can cause poor visibility. In the atmosphere, SO_2 and NO can form fine aerosol particle with a diameter less than 2 μm, containing sulphates and nitrates through the gas-particle conversion. Studies in the US had shown that in the urban area, the majority of sulfates in the air have particle sizes of less than 2 μm but the peak in the size distribution is around 0.2 to 0.9 μm (Dzubay 1982). These fine particles significantly degrade visibility by scattering light since wavelength of visible light ranges between 0.4 to 0.8 μm.

Emission of NO_x is known to be a contributor to visibility impairment in the form of plume and hazes (Kotchmar et al.1996). Although Kotchmar indicated that nitric oxide (NO) is an optically inactive gas which means that it does not affect atmospheric visibility, but when it oxidizes to become nitrogen dioxide (NO_2) which is a gas that absorbs light, chiefly at the blue end of the visible spectrum. Nitrogen oxides also play a significant role in the aesthetic impact due to its ability to cause yellow-brown discoloration on buildings and vehicles.

1.3 Air Pollution concerns in Malaysia

In Malaysia, air quality monitoring is carried out by the Department of Environment (DoE) by placing 51 monitoring stations at strategic locations all over the country (DOE Report 2009). The air quality status is reported in terms of Air Pollutant Index (API). The air pollutants used in computing the API are ground level ozone (O_3), nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and particulates of less than 10 micron in size (PM_{10}). The strategy is to monitor air quality at high population and high traffic areas. Air pollution comes from either static or moving sources as defined by the Department of Environment Malaysia. Table 1.1 shows the contributions of pollutants to the emission load for the year 2006 – 2012.

Table 1.1. Malaysian Air Pollution Load from all sources (metric tonnes)

Year	NO_x	**SO_2**	**CO_2**	**PM_{10}**
2006	393,209	194,265	1,368,243	29,978
2007	563,078	158,120	1,774,396	38,763
2008	409,972	161,913	1,451,746	31,672
2009	756,359	171,916	1,621,64	27,727
2010	740,006	174,820	1,681,440	26,964
2011	770,099	190,075	1,759,248	27,719
2012	877,364	198,519	1,873,730	NA

The Department of Environment (Malaysia) had categorized the main sources of air pollution in the country as:

- Mobile sources
- Stationary sources
- Open burning
- Trans boundary pollution

The first three categories represented the most significant contributors. Static sources were defined as those coming from factories, power stations, incinerators and other buildings and facilities. On the other hand, moving sources are mainly transportation such as cars, lorries and motorcycles. Open burning is frequently related to agricultural activities such as sugarcane and paddy field clearing. However, illegal burnings such as at landfill and private factories are also issues that need to be tackled by the DOE.

1.4 Contribution of NO_x emission from power generation and transportation in Malaysia

1.4.1 Contribution from power generation activities

For the purpose of this thesis, only mobile and stationary sources are highlighted. Table 1.2 shows the annual distribution (%) of emission load from the main sources from 2007 - 2012. Emission load from electricity generation has increased vastly from 16% in 2007 to 60% of the total load in 2012. On the other hand, the NO_x load for motor vehicles has dropped from 70% to 26% in the same period.

Table 1.2 Distribution of NO_x load by sources (%)

	2007	**2008**	**2009**	**2010**	**2011**	**2012**
Power plants	16	27	57	61	61	60
Motor vehicles	70	49	28	29	28	26
Industries	12	21	12	7	8	6
Other	2	3	3	3	3	8

Electricity generation in Malaysia is provided by either the public or private utility companies such as Tenaga National Berhad (TNB), Sabah Electricity Sdn Bhd and Syarikat SESCO Berhad. There are also 27 independent power providers (IPPs) throughout the country that supply their power through these utility companies. In addition to that, by 2012, there are 21 licensed renewable energy power projects taken by the private sectors (Suruhanjaya Tenaga 2012). Table 1.3 shows the installed capacity of these providers and the actual maximum demand of electricity for Peninsular Malaysia for the year 2007 to 2012. The maximum demand is the highest daily demand recorded in that particular year. The Energy commission had also stated that the energy demand in the country had increased steadily from 2007 to 2012, due to the economic recovery activities and climate change (weather) (Suruhanjaya Tenaga 2011, 2012).

Table 1.3: Energy supply and demand in Peninsular Malaysia.(MW)

	2007	**2008**	**2009**	**2010**	**2011**	**2012**
TNB Installed capacity	6346	6346	7040	7040	7054	9072
IPP Installed capacity	13377	13377	14777	14777	14763	12677
Maximum demand	13620	14007	14245	15072	15476	15826

Different types of fuels are used to generate electricity as shown in Tables 1.4a and 1.4b. Fossil fuels namely gas, coal and diesel are still the most used and eventually the main contributors to the NO_x emission load. The power stations are either thermal or hydro power. The thermal power stations use different type of generation such conventional thermal, thermal coal, combined cycle gas turbine and open cycle gas turbine, each using a single type or combined fuels. Diesel generators are only found in Sabah.

Table 1.4a. Installed capacity by fuel type (%) for 2007 - 2012

Fuel type	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
Gas	57.00	57.40	53.70	55.52	51.58	52.93
Coal	24.10	25.00	27.70	28.26	27.01	26.64
Hydro	8.40	8.50	7.60	7.78	10.60	11.51
Diesel	5.00	5.90	5.50	4.70	5.28	5.47
Oil	1.30	0.60	0.40	0.95	2.85	0.62
Biomass	2.20	2.30	4.80	2.47	2.60	2.66
Others	2.00	0.30	0.30	0.32	0.07	0.14 (Solar 0.03)
Total capacity (MW)	**24,821.00**	**24,608.00**	**27,700.00**	**27,179.00**	**28,433.00**	**28,824.00**

Table 1.4b : Generation by fuel type (%) for 2007 - 2012

Fuel type	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**
Gas	62.60	62.80	59.00	52.16	43.86	45.49
Coal	28.40	27.30	32.40	39.41	41.16	41.48
Hydro	5.60	6.90	5.10	5.11	6.34	6.9
Diesel	2.40	2.10	2.20	1.25	4.02	3.24
Oil	0.10	0.10	0.10	0.18	3.38	1.7
Biomass	0.70	0.70	1.10	1.10	1.21	1.12
Others	0.20	0.10	0.10	<0.20	0.03	0.06 (Solar 0.01)
Total generation (GW)	**108,539**	**113,823**	**116,114**	**125,045**	**127,069**	**134077**

The type of fuel used in the generation determines the composition of the flue gases. The typical compositions of flue gases from some of the fuels are shown in Table 1.5 (Zevenhoven, 2001). From the table, it can be seen that combustion of coal and gas fuels contributed high amount of NO_x to the environment.

Table 1.5: Typical composition of some raw flue gases

	Pulverized Coal combustion flue gas	**Coal gasification flue gas**	**Coal-fired IGCC flue gas**	**Gas-fired CC flue gas**
O_2 %-v	~ 6		~ 12	~14
N_2 %-v	~ 76	~4 / ~1	~ 66	~76
CO_2 %-v	~11	~4 / ~13	~ 7	~ 3
H_2O %-v	~ 6	~4 / ~1	~ 14	~ 6
CO %-v		~58/~40		
H_2 %-v ,				
Ar %-v	~ 1	~ 1	~ 1	~1
SO_2 ppmw			10 – 200	
H_2S ppmw		1000-4000		
NO_x ppmw	500 – 800		10 - 100	10 - 300
NH_3 ppmw		300 – 800		
HCN ppmw		40 – 150		
HCl ppmw		500 – 600		
HF ppmw		150 – 250,		
dioxin ppb	<< 1,			
CH_4 %-v				
CnHm %-v				
Hg ppmw	0.1 – 1	0.01 - 0.1		
Cd ppmw	0.01 – 1	0.01 - 0.2		
other heavy metal ppmw	0.5 – 2	~ 20		
dust g/m^3	5 – 20	~17 / ~8	<< 0.02	

Figure 1.1 shows the relationship between the total generated electricity and NO_x emission from power plants in Malaysia. As stated earlier, the country's energy demands increase steadily between the 2007 – 2012 periods. The NO_x load had also increased with actual electricity generated although non-linearly. Between the years 2008 to 2009, there was a sudden increase in the NO_x load. As earlier seen in Table 1.4a where it indicates that the installed capacity of coal type plant had increased by almost 3% from 2008 to 2009. The generation from coal type plant had increased by 5% for this period as previously shown in Table 1.4b. It was uncertain if this could be the main reason for the sudden increase, but it can be concluded that it had contributed significantly to the pollution.

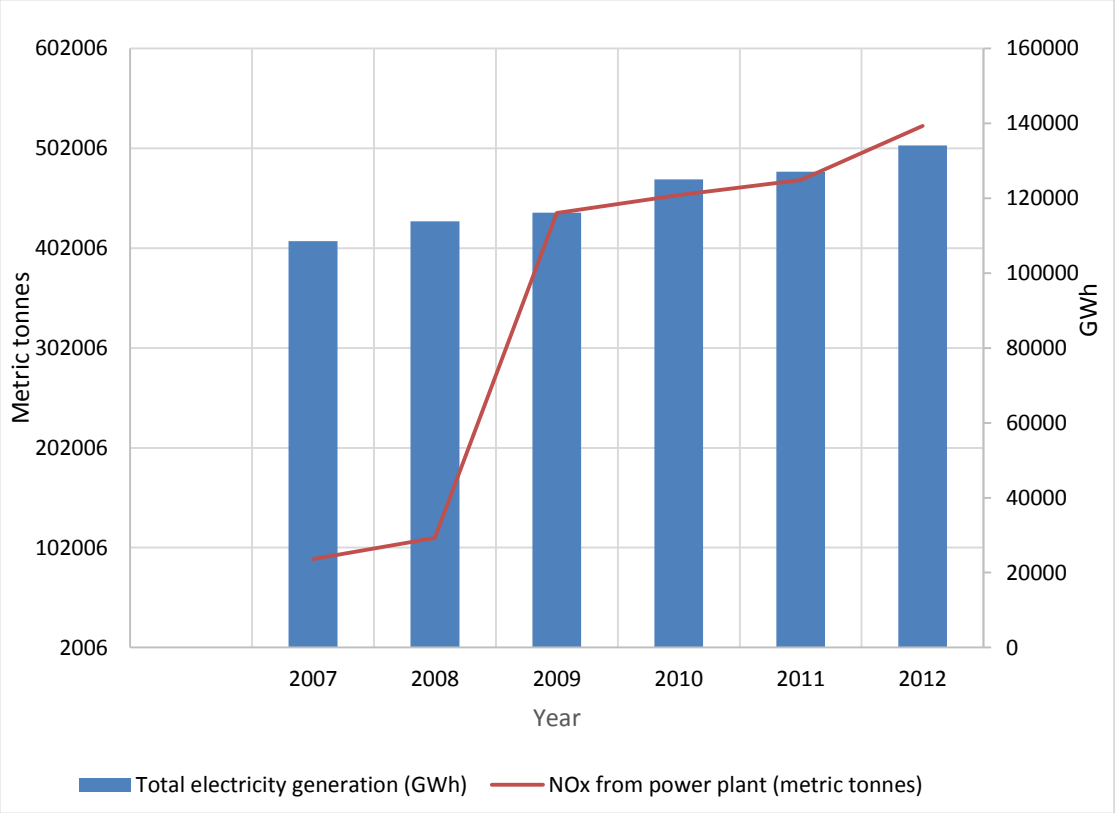


Figure 1.1: Relation between the total generated electricity and NO_x emission from power plants in Malaysia

1.4.2 Contribution from transportation

According to the statistic given by the Road Transport Department (Malaysia), there are more than 21 million registered vehicles up to the year 2012. The biggest number is motorcycles followed by motorcars (Table 1.6). These vehicles had been the major contributors to air pollution in the country. Emission of smoke and gaseous pollutants such as carbon monoxide, hydrocarbons, oxides of nitrogen and particulate matters emitted from motor vehicle exhausts are controlled under the Environmental Quality (Control of Emission from Diesel Engines) Regulations, 1996 and the Environmental Quality (Control of Emission from Petrol Engines) Regulations, 1996. Most vehicles in the country use fossil fuel either as petrol or diesel and most recently natural gas. Electric or hybrid cars are still low in number although the government had imposed no import tax to promote its usage.

Table 1.6 Accumulated numbers of registered vehicles/ transportation up to 2011

Vehicle	**Total registration**	**Percentage**
Motorcycles	9,985,308	46.66
Motorcars	9,721,447	45.42
Commercial vehicles	997,649	4.66
Public transport	180,998	0.85
Others	515,867	2.41
Total	**21,401,269**	**100.00**

The relationship between the number of registered cars and the amount of NO_x emission load can be seen in Figure 1.2. Prior to 2008, the amount of NO_x had increased significantly with the number of vehicles. However, the amount had dropped in 2008 although the number of registered vehicles remained increasing. A possible reason for this could be explained by the Asian Development Bank's Clean Air Initiatives for Asian Cities.

Under the Asian Development Bank's Clean Air Initiatives for Asian Cities (Discussion Draft 2006), it was cited that Malaysia adopted Euro 1 emissions standard for new light-duty vehicles in 1997, and Euro 2 standards for gasoline vehicles in 2000. It was also reported that Euro 2 was introduced for diesel vehicles in 2007. The Euro 3 standard for

gasoline vehicles was introduced in first quarter of 2009. This means that stricter measures had been taken to control emission from motor vehicles.

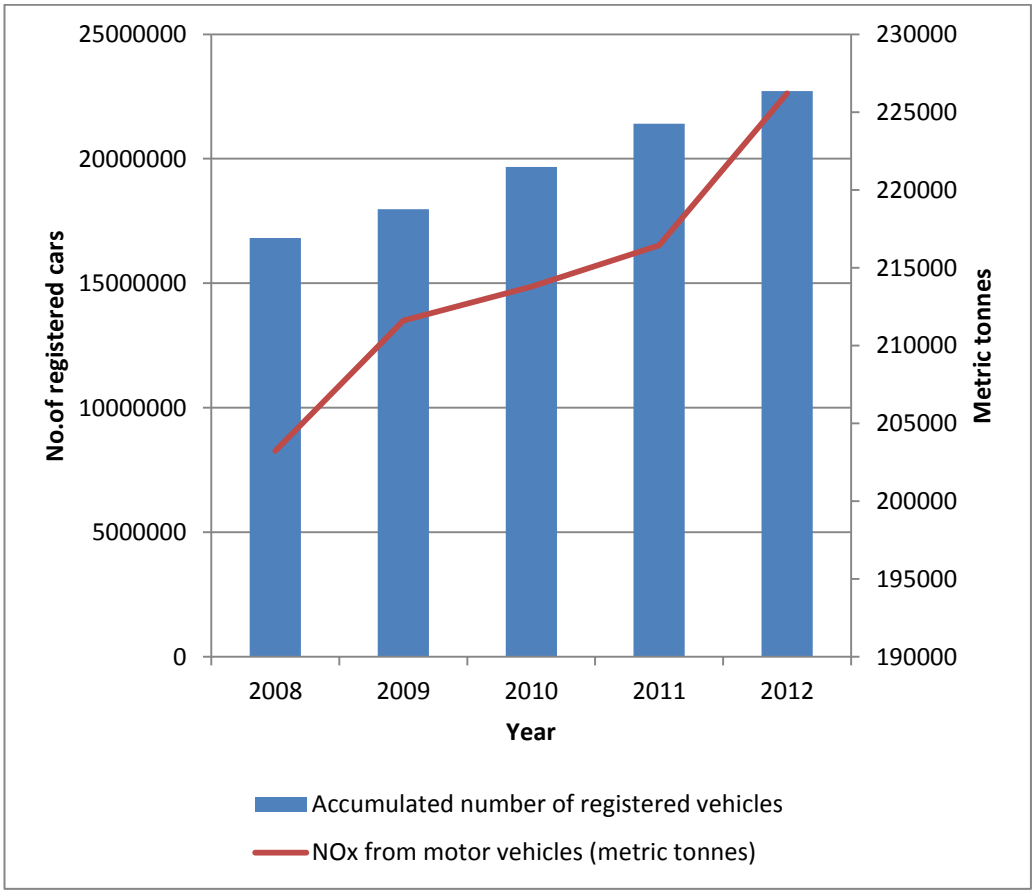


Figure 1.2: Relationship between the number of registered cars and the amount of NO_x emission load.

1.5 Control of NO_x

It is important to have some understanding on how NO_x are formed before designing its control method. In combustion processes, NO_x is formed via the following mechanism:

a. Thermal NO_x

This is a thermally dependent process where at high-temperature nitrogen reacted with oxygen by the Zeldovich mechanism:

$$N_2 + O_2 \rightarrow NO, NO_2$$

Higher temperature will increase NO_x especially when the combustion air in a furnace, for example, is preheated.

b. Fuel NO_x

Fuel NO_x is formed by the direct oxidation of organo-nitrogen compounds contained in the fuel. During the combustion, the nitrogen bound in the fuel, such as coal and oil, is released as free radical and forms free N_2 or NO.

c. Prompt NO_x

In this mechanism, atmospheric nitrogen reacts with radicals such as C, CH and CH_2 fragments derived from fuel. The reaction is relatively fast hence the name prompt. Prompt NO_x is less important compared to the other mechanism especially at higher temperature.

It should be noted that the terms thermal NO_x, fuel NO_x and prompt NO_x are normally used by US EPA or within the fuel and its related industries. The US EPA had outlined the developed techniques to control NO_x from stationary sources, in its document, US EPA 450/1-78-001 and US EPA 456/F-99-006R. The techniques were categorized

based on the basic principle involved in the system. Some of the techniques are used as preventive measures while other as add-on to do the cleaning methods. (Table 1.7)

Table 1.7: NO_x Control Methods

Abatement or Emission Control Principle or Method	**Successful Technologies**	**Pollution Prevention Method or Add OnTechnology**
1. Reducing peak temperature	Flue Gas Recirculation (FGR)	Prevention
	Natural Gas Reburning	Prevention
	Low NO_x Burners (LNB)	Prevention
	Combustion Optimization	Prevention
	Burners Out Of Service(BOOS)	Prevention
	Less Excess Air (LEA)	Prevention
	Inject Water or Steam	Prevention
	Over Fire Air (OFA)	Prevention
	Air Staging	Prevention
	Reduced Air Preheat	Prevention
	Catalytic Combustion	Prevention
2.Reducing residence time at peak temperature	Inject Air	Prevention
	Inject Fuel	Prevention
	Inject Steam	Prevention
3. Chemical reduction of NO_x	Fuel Reburning (FR)	Prevention
	Low NO_x Burners (LNB) Selective	Prevention
	Catalytic Reduction (SCR)	Add on
	Selective Non-Catalytic Reduction (SNCR)	Add on
4. Oxidation of NO_x with subsequent absorption	Non-Thermal Plasma Reactor	Add on
	Inject Oxidant	Add on
5. Removal of nitrogen	Oxygen Instead Of Air	Prevention
	Ultra-Low Nitrogen Fuel	Prevention
6. Using a sorbent	Sorbent In Combustion Chambers	Add on
	Sorbent In Ducts	Add on
7. Combinations of these Methods	All Commercial Products	Prevention and Add on

Before a pollution control system can be designed, there are several issues that must also be considered especially when dealing with gaseous pollutants. Appendix A gives a more detailed chart where screening can be made based on the description of each technology. This chart was adapted from Baukal (2004). Each technology is presented with its potentials, cost summary, efficiency and applicability. Gaseous pollutants commonly contained multiple pollutants such as SO_2, NO_x, CO_2 and hydrocarbons, to name a few. Therefore, multiple technologies may be needed to handle multiple pollutants. Sometimes, the chosen technique may generate other pollutants while destroying the targeted one.

In general, there are four basic strategies to control or reduce NO_x (Baukal, 2004 and Bradford, 2002):

a. Pre-treatment

This is a preventive technique to minimize the generation of NO_x. The incoming feed materials are treated to reduce the NO_x. For example, partially or completely substituting natural gas for fuel oil can often significantly reduce NO_x emissions by reducing the amount of nitrogen in the fuel. Switching from air to pure oxygen for combustion can eliminates almost all nitrogen from the process. The strategy is to reduce or eliminate nitrogen either in the fuel or feed materials.

b. Process modification

There are many techniques that can be used to modify processes to reduce NO_x emission. One example is by reducing firing rate when the mass of NO_x emitted from the plant is too high. By reducing the firing rate, less fuel is consumed and hence less NO_x is formed. However, this may affect the production rate. In some cases, it may be possible to replace gas-fired equipment with electrically heated units that do not produce NO_x. This may be costly since the electrical tariff is normally higher compared to fuel price. Improving thermal efficiency is more popular method as it reduces pollution but at the same time uses less fuel that translates into better operating cost.

c. Combustion modification

One of the most-popular methods in this strategy is to replace existing burner with low NO_x types. The designs of such burners incorporate a variety of technique for reducing NO_x such as air and fuel staging, water or steam injection and ultra-lean premixing. Flue gas recirculation is also commonly used.

d. Post-treatment

Post treatment is where NO_x is reduced or removed from exhaust gases after it has already been formed in the combustion chamber. In general, reducing agent or scrubbers such as CO, CH_4, hydrocarbon or ammonia are used to remove the oxygen from the NO and convert it into N_2 and O_2. Some catalyst may be required in the process. Two of the most common methods of post-treatment are

selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). In recent years, plasma related techniques are also being studied and implemented. The most successful is the electron beam flue gas treatment (EBFGT) where energized and accelerated electrons are used to supply radicals that will react with the pollutants. Silent discharge or dielectric barrier discharge also provides energized electrons but at a smaller scale.

1.6 Rationale of the study

As seen in the statistics provided by the DoE Malaysia, there are positive and negative stories concerning the NO_x emission load. On the positive side, the emissions from motor vehicles have been successfully reduced by adapting to the stricter Euro standards for fuel. Better designed cars had improved the combustion of fuel and hence exhaust gases are far less toxic as compared to previously. However, the demand for energy due to vigorous economic recovery activities had eventually caused higher NO_x emission from electricity generations. Post treatment to control NO_x deemed most suitable for many power stations as it is possible to install the additional treatment system to fit the current setup.

There are many ways to abate or control emission of NO from fossil fuel combustions as discussed earlier and summarized in Appendix A. In addition to the methods described; there have been many successes in the implementation of plasma-based remediation of flue gases. Electron beam flue gas treatment system has been proven to be able to remove SO_2 and NO_x simultaneously from coal-fired emission as reported by Namba (1993, 1995), Matzing (1992, 1996), Chmielewski (2003, 2004) and Licki

(2013). Several industrial-sized systems have been installed in Poland, Japan and China. However, the issues such as high power consumptions and high capital are still the main concerns for power generation companies to accept the technology. The system is also not economical to be installed in smaller factories or diesel fired stacks.

In this study, the electron beam processing is used to remediate emission from diesel combustion. Currently, the EBFG installations worldwide were designed to treat emission from coal combustion. The installation in Nuclear Malaysia is the only one in the country and it was dedicated for diesel emission which makes it a unique set up. It should also be noted that the optimization work is exclusive for each installation since the setup is different.

Although the majority power stations use coal, gas or mixed fuel, diesel is still an option due to its combustion performance. At a smaller scale, commercial ships are run on diesel engines and currently there are not many efforts to control the emission in the sea. A study on the possibility of using the EB flue gas treatment for diesel engine may have its novelty since this is not being tested at other places. Currently, most studies are focused on simultaneous removal of SO_2 and NO_x. Diesel emission also contains volatile organic compounds and other hydrocarbons which are persistent pollutants that are not easily removable. Thus with the current installation, studies on treatment of volatile organic compounds (VOC) and other hydrocarbons can be carried out.

The idea of using the dielectric barrier discharge reactor came about when it was used to produce ozone to treat wastewater from the textile industry, in particular, to remove the

colors (Ramasamy et. al., 2001). The ability of the reactor to produce ozone (O_3) from O_2 indicates that it can also produce O radical that can further react with other gases. Apparently, there are also several works that have proven that this can be done. However, each work has different design and efficiency. The proposed reactor is modular, making it easy to upscale to suit the processing flow rate. Although the feed gases used in the experiments are not the same as diesel combustion, the similarity is on the high concentration of NO which is the main pollutant. This study also tries to find the best condition for the reactor to function in reduction mode or suppress oxidation. The resulting set up will eliminate post treatment.

1.7 Objectives

The main objective of this research is to establish methods of removing nitric oxides using plasma related techniques. The main ingredient of the techniques proposed is energized electrons that are generated either by an electron beam machine/accelerator or a dielectric barrier discharge reactor. The more structured objectives of this project are:

1. To remove NO using electron beam
2. To remove NO using dielectric barrier discharge reactor
3. To find conditions that affect the removal efficiency in both methods
4. To find the optimum condition for NO removal in both methods

CHAPTER 2:

REMOVAL OF NO_X IN GAS PHASE USING NON-THERMAL PLASMA TECHNIQUES

This chapter explains how the highly energetic electrons produced by electron beam machine or dielectric barrier discharge reactor interact in a gaseous environment. Some gas phase reactions that involve the oxidation and reduction of NO in the gas stream are presented. The final product recovery mechanism is also explained. The reactions mechanisms shown may not necessarily represent the complete process due to the complexity of NO remediation. At the same time, the mechanisms listed are based on research completed in the field of atmospheric chemistry. The principles behind gas phase removal are almost similar although it differs in concentrations of the species, temperature and pressure of the gas stream.

Plasma oxidation is the key process mechanism applied in this study. The two methods of producing radicals in gas phase environment are also described.

2.1 Non-thermal plasma

Non-thermal plasma refers to plasmas that are not in thermodynamic equilibrium, which means that the electron mean energy is much higher than the ion and gas mean energies (US Patent # 6,852,200 2005). Both electron beam irradiation and electrical discharge methods can produce non-thermal plasmas (Penetrante 1997, Ighineanu 2005 and Chen 2002). The basic principle that underlies these methods is to produce plasma in which the majority of the electrical energy goes into the production of energetic electrons rather than into atmospheric gas heating. Under the atmospheric pressure conditions, the electrons are normally short-lived and may not collide with the targeted pollutants. However, they may undergo collision with the dominant background gas molecules and hence produce radicals through the electron impact dissociation and ionization. In the gas phase, reactive gas species such as OH (hydroxyl), HO_2 (hydroperoxyl) and O radicals are generated and can then be utilized to oxidize the NO_x molecules.

2.2 Gas phase removal process of nitric oxide, NO

The efficacy and practicality of removing NO from flowing gases depend on the reaction rates of NO with the reactive radicals produced by the non-thermal plasma process. Equation (2.1) is the general form of this process: (2.1)

$$A + B + M \rightarrow AB + M \qquad (2.1)$$

In this equation, M is a third body, usually N_2 in the background. The actual elementary reactions involved in this process are as described in the following reactions:

$$A + B \leftrightarrow AB^{*} \qquad (2.2)$$

$$AB^{*} + M \rightarrow AB + M \qquad (2.3)$$

When A collides with B, it immediately forms AB^{*} which is the excited state molecule. AB^{*} then lose its energy during a collision with a third body M to form AB, which is a stable product. By applying a steady state approximation to the net rate formation of AB, the following equation can be derived to describe the concentration of AB^{*} (written as $[AB^{*}]$).

$$d[AB^{*}]/dt = k_1 [A][B] - k_{-1}[AB^{*}] - k_2[AB^{*}][M] = 0 \qquad (2.4)$$

hence:

$$[AB^{*}] = k_1 [A][B] /(k_{-1+} k_2[M]) \qquad (2.5)$$

Where; k_1 is the reaction rate constant for the forward reaction of 2.2

k_{-1} is the reaction rate constant for the reverse reaction of 2.2

k_2 is the reaction rate constant for the reaction of 2.3

By definition of reaction rate, d[AB]/dt, the following is derived

$$d[AB]/dt = -d[A]/dt = -d[B]/dt = k_2[AB^*][M]$$

$$= k_1k_2[M][A][B]/(k_{-1} + k_2[M]) \qquad (2.6)$$

For estimation purposes,

if $k_2[M] << k_{-1}$, then $d[AB]/dt = k_1k_2[M][A][B]$

if $k_2[M] >> k_{-1}$, then $d[AB]/dt = k_2$ (which is the forward reaction rate constant for 2.2)

Equation (2.6) can be used to calculate the reaction rate for a gas phase reaction if the concentrations of the reacting species and the reaction rate constants are known.

2.3 Reaction mechanism in the plasma remediation of nitric oxide

Nitric oxide is generally a reactive scavenger that will react rapidly with OH, HO_2, O_3, N and O as shown in the following reactions:

Reaction mechanism,	**k (cm^3/molecules s)**	**Equation number**
$NO + HO_2 \rightarrow NO_2 + OH$	6.6×10^{-12}	(2.7)
$NO + O_3 \rightarrow NO_2 + O_2$	1.8×10^{-14}	(2.8)
$NO + O + N_2 \rightarrow NO_2 + N_2$	1.0×10^{-31} (cm^6/$molecule^2$-s)*	(2.9)
$NO + OH \rightarrow HNO_2$	6.6×10^{-12}	(2.10)
$NO + N \rightarrow N_2 + O$	2.2×10^{-11}	(2.11)
$NO_2 + OH \rightarrow HNO_3$	1.1×10^{-11}	(2.12)
$NO_2 + O \rightarrow NO + O_2$	5.0×10^{-12}	(2.13)
$NO_2 + O_3 \rightarrow NO_3 + O_2$	2.8×10^{-17}	(2.14)
$NO_3 + NO_2 \rightarrow N_2O_5$	3×10^{-12}	(2.15)
$N_2O_5 + H_2O \rightarrow 2\ HNO_3$	5×10^{-21}	(2.16)
$2HNO_2 \rightarrow NO + NO_2 + H_2O$	1.2×10^{-17}	(2.17)
$HNO_2 + hv \rightarrow OH + NO$	**	(2.18)

* Three body reaction

Note: These reaction mechanisms were extracted from the compilations made by Gentile 1995, Chang M.B.,1992 and Baulch 1982)

The product of reactions from (2.7) to (2.9) is NO_2 that is subsequently oxidized by the OH radical to form HNO_3 (reaction 2.12). The NO_2 can also reform NO when it reacts with O (reaction 2.13) or it can form NO_3 when reacting with O_3. (2.14). The NO_3 from 2.14 then react with NO_2 to form N_2O_5 which when hydrolyzed through reaction 2.16, will form HNO_3. The end product of reaction 2.10, HNO_2 is not as stable and hence will decompose as in reaction 2.17. This will occur at temperature of above 100° C. It can also be decomposed through photolysis at wavelength of light less than 400nm (Watson 1988).

There are many more ways or reaction mechanisms that may influence the gas oxidation of NO to HNO_3. The pathway is complicated since NO can be removed and can be formed again in the presence of O_2, N_2 and $H_2O_{(g)}$ as shown in the previous reactions. The complexity of the reaction pathways for plasma remediation of N_xO_y are shown in Fig. 2.1 (from Gentile 1995, Baulch et al. 1982). The targeted pollutant in this study, nitric oxide (NO), is highlighted by the diamond and the major end products namely N_2, NO_2, N_2O, N_2O_5, HNO_2 and HNO_3 are boxed.

The reactions are assisted by radicals that are listed next to where the corresponding reaction arrows are. The radicals are produced either through electron beam bombardment or the discharge in a dielectric barrier.

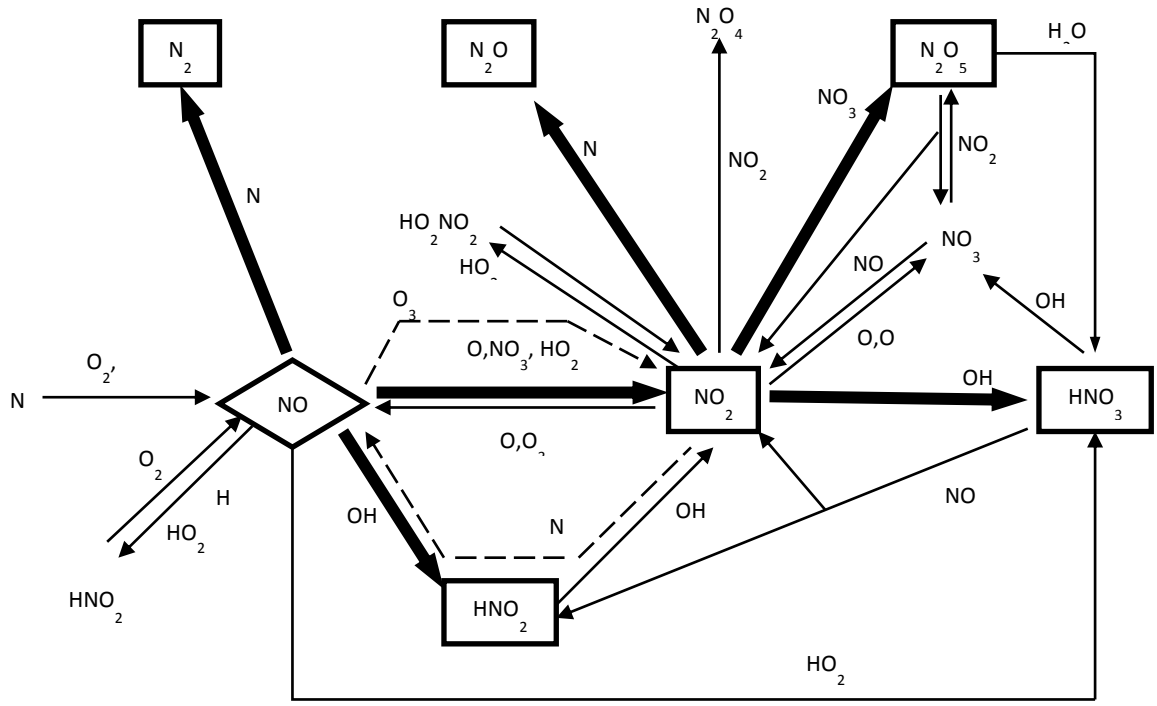


Figure 2.1 Dominant reaction pathways that may occur during plasma remediation of N_xO_y

The two main pathways for remediation of NO are:

Reduction: $NO + N \rightarrow N_2 + O$

and

Oxidation : $NO + O \rightarrow NO_2$

$NO_2 + OH \rightarrow NHO_3$

The preferred pathway is dependent on the desired end product. For example, the case where acidic waste product can easily be collected for further treatment then the oxidation pathway is acceptable. This is possible for installations in stationary sources

such as power stations. In smaller installation or for mobile sources, reduction pathway is much preferred since the end products N_2 and O can be discharged directly to the atmosphere.

The reduction pathway although preferable may not be easy to achieve since O_2 and water vapor are byproducts from the combustion of fossil fuel. Therefore, drying may be necessary as pretreatment. The drying process in turn will increase the electricity consumption of the system.

Through the oxidation pathway, the end product HNO_3 can exist in either liquid or gaseous form due to its relatively high equilibrium vapor pressure of about 215 mm Hg at 50° C (Perry et al., 1984). The final state of the product would depend on its concentration and the gas temperature and pressure. It is possible to neutralize this acid by injecting gaseous ammonia ($NH_{3(g)}$) in a stoichiometric ratio of one to form ammonium nitrate NH_4NO_3. This was proven effective when included in the EB treatment for flue gas emitted from coal-fired power station (Frank 1990, Chmielewski 1997, 2002, Basfar 2010, Liscki 2013). Hence, removal of NO from gas streams can be done via gas phase oxidation and reduction processes as described by the reactions presented and previous researches. These reactions will occur in the presence of gas phase radicals.

2.4 Generation of gas phase radicals.

Plasma excitation is one of the efficient ways to generate gaseous radicals (Fridman 2008, Kimura 2000). In this process, electrons are accelerated in an electric field to gain sufficient energy to excite, ionize and dissociate gas molecules in a gas stream to form gas phase radicals. There are many ways to create the plasma excitation that generates gas phase radicals. Two methods, namely electron beam and dielectric barrier discharge, are presented and used in this thesis. The methods will be applied for different scale of processing relative to the size of reactors used. The gas phase reactions governing the oxidation of NO will follow the reaction chains described earlier. However, the electron kinetics may differ between the electron beam environment and the electrical discharge environment.

2.4.1 Electron interaction with the gas in electron beam environment

Energized electrons have limited penetrating power in matter, and this characteristic is somehow useful for gaseous processing. The low-density gaseous medium contains light nuclei and hence during collision the electron will dissipate its energy mainly through interactions with the orbital electrons causing ionization or excitations. The incident energy will be distributed over a large volume of the gas.

The electron range R is defined as the linear distance from the electron source at which the average electron energy has decayed to a few percent (<5%) of the starting value. For electron energy E between 300 and 800 keV, R is proportional to $\rho E^{1.35}$, where ρ is the density of the material. (Matzing 1992). Thus, the electron range varies between 0.5 – 2.5 m for incident energies of 300 and 800 keV, respectively, in gases at ambient condition. This range of energies was used in the earlier studies of electron beam treatment of flue gases (Tokunaga 1992, Namba 1993 , Penetrante 1993).

The electrons will also lose energy through the interactions with electron shells of the molecules at energies below 1 MeV. The energy transfer through a single collision varies between few eV to some tens of keV and may leave the contact molecules in excited states. If more energy is transferred to a molecule than required for dissociative ionization, the excess energy will mainly be taken up by the secondary electrons released in the ionization process. The secondary electrons may cause the same excitation and dissociation process as the incident primary electrons until they become thermalized. In the flue gas, the absorbed energy is proportional to the mass fraction of the components in the gases (Chmielewski 1997). Hence, more than 99% of the energy is usually absorbed by nitrogen, oxygen, water vapor and carbon dioxide in the flue gas (Matzing 1992, 1996).

During the electron beam processing, the efficiency for a particular electron impact process can be expressed in terms of the *G*-value that is defined as:

$$G\text{-values} = 100N_j/\varepsilon_p$$

Where N_j is the number of dissociation or ionization events and ε_p is the primary electron energy. The primary radiolysis products formed from these gases have been measured quantitatively by Willis and Boyd (1976). Matzing (1992) had also derived the following stoichiometric equations from the measurement of the radiolytic gain (*G* value) of primary reactive species formation, per 100 eV absorbed energy:

$$4.43\ N_2 \xrightarrow{100\ eV} 0.29\ N_2^* + 0.885\ N\ (^2D) + 0.295\ N\ (^2P) + 1.87\ N\ (^4S) + 2.27\ N_2^+ + 0.69\ N^+ + 2.96\ e\text{-}$$

$$5.377\ O_2 \xrightarrow{100\ eV} 0.077\ O_2^* + 2.25\ O\ (^1D) + 2.8\ O\ (^3P) + 0.18\ O^* + 2.07\ O_2^+ + 1.23\ O^+ + 3.3\ e\text{-}$$

$$7.33\ H_2O \xrightarrow{100\ eV} 0.51\ H_2 + 0.46\ O\ (^3P) + 4.25\ OH + 4.15\ H + 1.99\ H_2O^+ + 0.01\ H_2^+ + 0.57\ OH^+ + 0.67H^+ + 0.06\ O^+ + 3.3\ e^-$$

$$7.54\ CO_2 \xrightarrow{100\ eV} 4.72\ CO + 5.16\ O\ (^3P) + 2.24\ CO_2^+ + 0.51\ CO^+ + 0.07\ C^+ + 0.21\ O^+ + 3.03\ e^-$$

The *G*-values for the reactions presented in the above equations are in the range of 6 ± 2 per 100 eV which corresponds to radiolysis of 25 ± 10 ppm of gas molecules per kGy of radiation dose received (Matzing 1992, Chmielewski 1997). The *G* values may be varied by the additional chemical processes that can take place or incite during the irradiation.

In an electron beam irradiated environment, a large portion of the input power is consumed by the dissociation and ionization of molecules. Only 6% or less power is dissipated in vibrational excitation of the N_2. Penetrante (1993) had tabulated the energy dissipation in plasma produced by electron beam irradiation of dry air as reproduced in

Table 2.1. Some of the excited atoms and molecules react rapidly with the background molecules to produce additional dissociation. Excited oxygen atoms $O(^1D)$ for example react rapidly with H_2O to form additional OH radicals. The positive ions will mostly react to produce additional O_2^+ ions, which then also react with H_2O to form additional OH radicals. This is how EB method differs from the discharge method of producing OH radicals. In EB environments, they are predominantly formed from positive ions whereas in discharge reactor; the OH radicals are formed both from direct dissociation of H_2O by electrons and excited oxygen atoms.

Table 2.1: Energy dissipation in the plasma produced by electron-beam irradiation of dry air (80 % N_2 + 20 % O_2)

Process	**Energy Dissipation(% of Input Power)**
N_2 Vibrational	5.3
$N_2(A^3\sum_u^+)$	1.1
$N_2(B3\prod_g)$	1.8
N_2 Dissociation	24.0
N_2 Dissociative Ionization	13.9
N_2 Molecular Ionization	28.3
O_2 Vibrational	0.6
$O_2(a^1\Delta_g)$	0.7
O_2Dissociation	8.3
O_2 Dissociative Ionization	2.9
O_2 Molecular Ionization	2.8
Others	10.3

2.4.2 Electron beam flue gas treatment

The studies on utilizing electron beam irradiation process to treat flue gases containing SO_2 and NO_x was first initiated by the Japan Atomic Energy Research Institute and the Tokyo University in the 1970s and 80s (Tokunaga et al. 1977, 1978). The principle behind this technology was based on the observation of the chemical reaction of gas phase radicals that caused the formation of photochemical smog in the troposphere (Leonhardt, 1993). The reactions that take place in the troposphere are very similar to those in the irradiated gas, but the EB process is run at a much higher energy level and under controlled conditions. The EBARA Corporation had played important roles in the technical development of an upscale facility to treat SO_2 and NO_x simultaneously. In 1977, they joined the effort with Nippon Steel to build a facility to treat 10,000 Nm^3/h of flue gas emitted from a steel sintering plant (Markovic, 1987). Later in 1992 another test facility was built in Nagoya, Japan, at the Chubu Electric Company coal-fired power station (Frank 1990, IAEA Bulletin 1/1994).

The simultaneous removal of SO_2 and NO_x using EB was further investigated by other researchers, financed by big corporations that led to several installations of demonstration and industrial plants as compiled in Table 2.2. There are also other installations but mostly as demonstration or pilot plants. As can be seen from the table, the EBFG was used to treat emission that contained high SOx compared to NO_x at ratios of 2:1 up to 4:1. All power stations listed in the table use coal as the main fuel, thus explaining the high SOx content in the emission. It should be noted that three of the four installations function at radiation dose less than 5 kGy. The removal efficiencies are,

therefore, more favorable for SOx compared to NO_x. The Pomorzany plant in Poland had installed four units of 300 kW EB machines (total of 1200 kW) and had achieved 90% and 70% removal of SO_2 and NO_2 respectively. The Beijing installation, although using even high power EB machines was only able to attain 90% and 20% removal of SO_2 and NO_x respectively. This shows that apart from the power requirements, the removal rate also depends on the initial concentrations of the pollutants in the flue gases. Each installation is expected to have its flue gas profiles, power requirement and removal efficiency. Therefore, any new installations may not necessarily achieve the same results as other plants, even with similar setups.

Table 2.2 Commercial EB flue gas treatment plants in the world.

	Chengdu	**Pomorzany Poland**	**Hangzhou China**	**Beijing China**
Year of installation	1997	1999	2002	2005
Boiler Power/ fuel	90MW / coal	130MW /coal	90MW /coal	150MW/ coal
Flue gas flow	300,000 Nm^3/h	270,000 Nm^3/h	305,400 Nm^3/h	630,000 Nm^3/h
Inlet SOx / NO_x	1800ppm/ 400ppm	525ppm/ 292ppm	967ppm/ 200ppm	1470ppm/ 583ppm
SOx/ NO_x removal	80% / 20%	90%/ 70%	85%/55%	90%/ 20%
Dose	3 kGy	8 – 12 kGy	4 kGy	4 kGy
EB accelerator	800 kV/ 400mA x 2	800 kV/ 375mA x 4	800 kV/ 400mA x 2	1000 kV/ 500mA x 2 1000 kV/ 300mA x 1
Process owner	EBARA	INCT	EBARA	IEPE

In Malaysia, the idea of having EBFG emerged as early as in 1993 after the management attended a Seminar on Electron Beam Technology for Environmental Conservation in Japan. The 3 MeV EPS-3000 was already in service at that time but mostly for research in sterilization and polymer cross-linking. However, it was not until 1998, a research collaboration agreement was made between Nuclear Malaysian and TNB Research to undertake the studies on utilizing the electron beam technology for purification of flue gases. A laboratory scale installation was designed with the assistance from IAEA experts to treat emission from a small diesel generator. The installation was completed and commissioned in 2002. Not many studies were done due to lack of experience and commitments from parties involved. In 2005, it was decided the project needed to be revived to obtain new results that may be used for future reference. It was acknowledged that works on EBFG treatment of flue gases from diesel combustion were still lacking. During the period from 2005 to 2006, some significant results were achieved. These results will be presented in this thesis. Due to increasing commercial demand for the irradiation time using the EPS 3000 and lack of funding for consumables, the EBFG project had to be stalled until present. However, the results obtained had shown that the flue gases from diesel emission can be treated using electron beam technology via plasma oxidation process.

2.4.3 Radical production in dielectric barrier discharge (DBD)

Dielectric barrier discharge is also known as silent discharge due to the absence of sparks, which are accompanied by local overheating, generation of local shock waves and noise (Fridman 2011). The discharges are characterized by the presence of at least one insulating layer in contact with the discharge between two planar or cylindrical electrodes connected to an AC power supply. Figure 2.2 shows typical configurations of dielectric barrier discharges; either in the planar or cylindrical forms (Kogelschatz 2002, Eliasson 1994, Fridman 2011). Typical clearance in the discharge gaps varies from 0.1 mm to several centimeters. The breakdown voltages of the gaps with dielectric barriers are practically the same as those between metal electrodes. Typically, if the gap is in the millimeters, the driving voltage at atmospheric pressure needed would be about 10 kV of AC voltage with a frequency ranging between 500 Hz to 500 kHz.

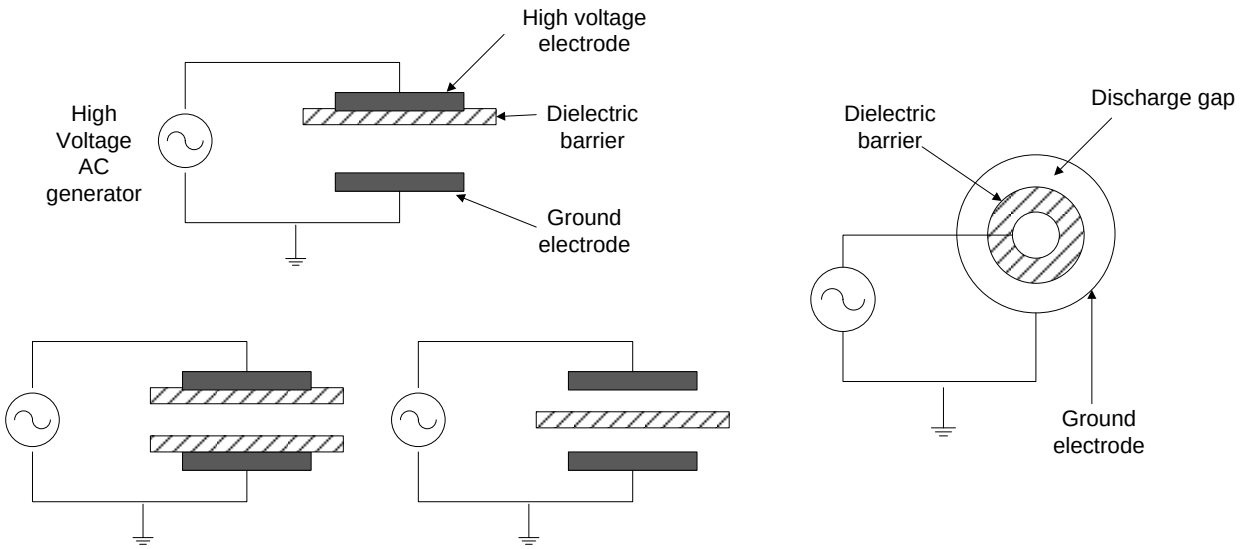


Figure 2.2: Typical dielectric barrier discharge configurations.

The dielectric material is usually chosen from those having high dielectric strength (V/mm) and high dielectric constant, such as glass, quartz or ceramic.

AC voltage is applied across the dielectric and the discharge gap. It should be noted that the DBDs cannot be operated with DC voltage because the capacitive coupling of the dielectrics necessitates an alternating electric field to drive a displacement current (Kogelschatz 2000). As the voltage increases towards the breakdown value, the gas within the gap become electrically conducting. At this moment, the existence of the dielectric material causes a stabilizing resistance leading to the formation of a large number of micro discharges of nanosecond durations (Eliasson 1997). A discharge will occur in the gap when the voltage reaches the breakdown voltage. It will cease or diffuse when the voltage recedes below that value. The micro discharges are defined to be in filamentary mode that is characterized as weakly ionized plasma.

The breakdown voltage for atmospheric air with a gap length between 0.01 and 20 cm can be calculated using the equation below (Meek and Craggs, 1978)

$$V_{so} = 24.4\ (\rho d) + \ 6.52(\sqrt{\rho d}),$$

where V_{so} is the breakdown voltage in kV, d is the electrode spacing in cm (or the gap) and $\rho = \left(\frac{p}{1013}\right) * \left(\frac{293}{T}\right)$ is the air density relative to its value at a pressure p = 1013 mbar and temperature T = 293 K (gas number density N = 2.51 x 10^{19} /cm^3). This is applicable for humidity of air at 11 g $H_2O_{(g)}$/m^3.

Meek and Craggs (1978) had further elaborated the equation by adding a correction factor k to include the humidity factor as below:

$$V_{sh} = V_{so}/k$$

Where, V_{sh} is the breakdown voltage at humidity of *h* (g/m3), at the same pressure and temperature. Therefore;

$$k = [0.051(h + 8.65)]^{-0.25}$$

The large electrical field excites the electron and hence ionizes or dissociates gas molecules to form partially ionized plasma. Gas phase radicals namely the OH, O and HO_2, are produced by these activities. The concentrations of these species are dependent on the magnitude and frequency of the applied voltage. Other physicals factors such as the arrangement configuration, gas flow and gas compositions will be investigated in this work.

The DBD has been widely used as ozone generator. However, there have been many works carried out to utilize the radicals produced by the DBD to oxidize pollutants such as SO_2 (Dhali & Sardja, 1991, Chang 1991), polyaromatic hydrocarbons (Ostapczuk 2008). NO_x removal has been studied by Chang (1992), Toda et al. (2001), Mok (2003) and Penentrante (1993) to name a few.

Sardja and Dhali (1990) had demonstrated that plasma chemistry alone is sufficient to convert SO_2 to H_2SO_4, where the plasma is being generated by a DBD reactor. Nearly 80% of SO_2 was removed from flue gas containing 775 ppm of SO_2. Chang (1991), on the other hand, treated the SO_2 by a combined DBD and plasma photolysis methods to

obtained more than 80% removal of SO_2. Simultaneous removal of SO_2 and NO_2 which are the major pollutants emitted from coal and oil combustion were also studied by Chang and his team from the University of Illinois USA, funded by the USEPA (Chang 1992). At constant moisture concentration, both SO_2 and NO removal efficiencies were found to increase with increasing temperature. At 160 °C with 15% by volume $H_2O_{(g)}$, more than 95% of the NO and 32% of SO_2 were removed from the gas stream. Niessen et al. (1998) had added ethane in the pre-treated gas mixture to enhance the removal efficiency. They discovered that a complete removal of NO can be achieved at an energy expense of 5 to 10 eV per NO molecule if 2000 ppmv C_2H_4 are present in the gas stream. Otherwise, 60 eV per NO molecule would be needed.

Established researchers such as Penetrante (1993, 1997) and Kogelschatz (1999) had contributed significant fundamental information regarding DBD and its application especially for environmental preservations and in particularly removal of gaseous pollutants.

In recent years, the interest to apply DBD for this purpose had rekindled especially for diesel engine exhaust treatment. Mohapatro (2012) had successfully removed 92% NO_x from diesel engine exhaust using DBD cascade with red mud catalyst operating at 400 °C. Wang et al. (2009) and Zhang (2007) had used the DBD to assist the selective catalytic reduction of NO_x by ethanol over Ag/Al_2O_3 catalyst. They proposed that the non-thermal plasma generated by the DBD was very effective for oxidizing NO to NO_2 under excess O_2 conditions and temperature ranging from 176° to 255 °C. Vinh et al., 2011, had carried out the fundamental study of NO_x removal from diesel exhaust gas using DBD, in Gunma University in Japan. The University of Malaya had established its low-temperature plasma laboratory where studies had been carried out to utilize the

DBD reactor for chemical synthesis. The DBD reactor had found its use to generate ozone to treat textile waste water (Ramasamy 2000, 2001). It was proposed that the same reactor to be used to remove nitric oxide from laboratory gas stream. In these studies, it was found that it is possible to sustain reduction pathway provided by the plasma chemical reaction:

$$NO + N \rightarrow N_2 + O$$

and preventing oxidation of the NO. Thus, post-treatment of the byproducts will not be necessary. The findings and discussions on this will be presented in later chapters.

CHAPTER 3:

METHODOLOGY 1:

ELECTRON BEAM FLUE GAS (EBFG) TEST RIG FOR REMOVAL OF NO_X FROM DIESEL COMBUSTION

The experiments in this study were carried out using two different methods. Two separate experimental setups were made at different locations. This chapter describes the electron beam flue gas (EBFG) treatment test rig that was installed at the ALURTRON Electron Beam Irradiation Facility, Malaysian Nuclear Agency in Bangi. This is a large scale laboratory test rig built to study the effect of irradiation on flue gases from diesel combustions. The installation was initiated as collaboration between Nuclear Malaysia and Tenaga Nasional R&D. The major components of the test rigs were tested individually before they were integrated into the test rig. The rig was tested as a complete system without initiating the electron beam irradiation before the actual experiments were carried out.

The second setup, described in Chapter 4, was a dielectric barrier discharge reactor that was built at the Plasma Technology Research Centre at the University of Malaya, Kuala Lumpur. The reactor was a desktop laboratory setup that was designed with simplicity and easy to use in mind.

3.1 Description of the EBFG Test Rig

The schematic diagram of the experimental setup is as shown in Figure. 3.1. A diesel generator set was used as the source of flue gas. Since the fuel was diesel, the emission was supposed to consist of high NO_x and almost zero SO_2 (measured values were around 10 ppm). The flue gas then flows through a static mixture vessel. At this point, any additional gas or gaseous compound could be added. A spiral blade inside the vessel was used to create natural mixing for the gases before entering the spray cooler. The main function of the spray cooler was to reduce the flue gas temperature and increase the moisture content by spraying fine water droplets into the gas flow. The gases travel along a piping system that was built through the thick bunker wall and into the process vessel. The process vessel was located right under the electron beam scanning horn where the irradiation occurred. The gases continued to leave the process vessel and exited through the bunker wall into the dust collector. It was expected that the during the irradiation and neutralization processes, dust-like particles will be formed. These particles were filtered through a bag filter for collection. The clean air left the test rig through the stack into the atmosphere.

The test rig was designed with the assistance from Prof. Dr. Chmielewski from the Institute of Nuclear Chemistry and Technology (INCT), Poland. The specifications of the test rig are summarized in Table 3.1.

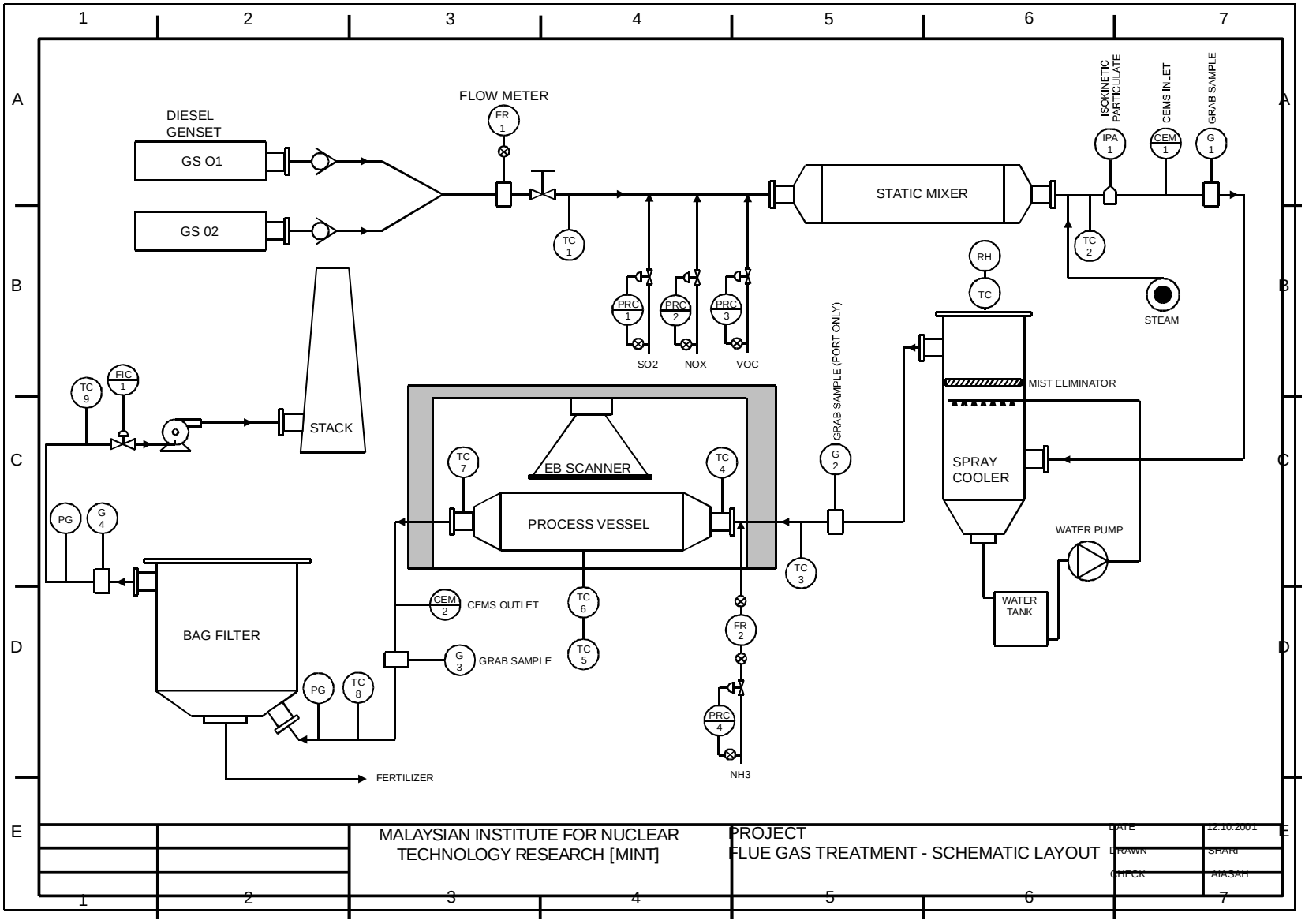


Figure 3.1: Schematic diagram of EBFG test rig installed at Nuclear Malaysia.

Table 3.1: Design values for EBFG.

Parameter	**Values**
Flow rate	400 Nm^3/hr
Temperature of gases at gensets outlet	150° C
Temperature of gases after spray cooler	60 - 70° C
Moisture content after spray cooler	10 – 15%
NO_x concentration at inlet	300 ppm (estimate)
SOx concentration at inlet	< 10 ppm (estimate)
Accelerator voltage	1 MeV (variable)
Beam Current	2 mA (variable)
Retention time (flow rate of 400Nm^3/h) inside vessel	1 sec
Estimated Dose	1.2 kGy

3.2 Specifications of the Electron Beam Machine

The electron beam machine EPS 3000 provided highly energetic electrons to react with the flue gases in the experiments. The specifications for the electron beam machine used in this project are as stated in Table 3.2.

Table 3.2: Specifications for Nuclear Malaysia's electron beam machine.

Machine	EPS-3000
Accelerator voltage	0.5 – 3.0 MeV
Beam Current	1–30 mA
Max beam Power	90 kW
Beam width/Area	30,60 and 120 cm
Dose Uniformity	± 5%

The EB machine is a DC type accelerator that can generate variable voltages and beam currents as stated in the specifications. This is an advantage to the experiment where observation can be made on the effect of variable current on the removal efficiency and to find the optimum EB condition for the required treatment. The accelerator voltage,

however, was fixed at 1.0 MeV, after considering the size of the process vessel and the electron penetration in the air. Although lower voltage is desirable, the machine could not operate continuously without triggering alarm. This was due to the condition of the machine itself that could not operate at lower than 1.0 MeV.

The process irradiation vessel was placed under the scanning horn inside the irradiation room. The electron beam was being scanned in the X and Y direction within the scanning horn after it left the vacuum environment into the atmosphere through a thin window. The distance between the scanning window and the vessel's window was kept at minimum to reduce any energy lost in the air. Both windows were made of titanium foil with 50 micron thickness.

Figure 3.2. Process vessel for flue gas treatment test rig.

3.3 Measurement of radiation dose

Direct measurement of the dose during experiment was not possible since there was no suitable dosimeter to do so. It was, therefore, necessary to carry out the measurement before the actual experimental works. The dosimetry work was done together with personnel from the Standard Secondary Dosimetry Laboratory (SSDL) of Nuclear Malaysia during the commissioning of the test rig.

The irradiation dose was measured using film type cellulose triacetate (CTA) dosimeters, a method that was also used by others such as Namba 1995 and as reported in the IAEA TECHDOC 1156 (2000). In our case we use Fuji Film's FTR-125 CTA as the dosimeter to measure the radiation dose delivered by the electron beam. The film contains 85% cellulose triacetate and 15% trifenile phosphate, by weight. The nominal thickness is 0.125mm which is suitable for high energy electron beam. The optical density will change after exposure to radiation. The absorbed dose was evaluated from the measured value of the increment of the optical density at the wavelength of 280nm using UV spectrophotometer. This dosimeter is commonly used for high dose measurement and as routine dosimeter in an electron beam facility.

A wooden rack was built to hold the CTA films. The rack was fitted inside the vessel where the irradiation was carried out. The CTA films were placed along the length of the vessel. The received or absorbed dose is dependent on the EB parameters used. For the dosimetry exercise, the selected parameters were accelerator voltage at 1 MeV and beam current of 2 mA. The SSDL had issued the results in the form of a short report and slides presentations for our reference. The report is as in Appendix B. The summary stated that the measured dose after 90 seconds of static irradiation was 111.96 ± 28.97 kGy.

The estimated absorbed dose received by the gas was dependent on the retention time inside the vessel. The retention time in this case refers to the period the gas resides inside the vessel while travelling from inlet to outlet point. It can be calculated from the volume of the vessel and the processing volume.

The dimensions of the process vessel are:

Inner radius = 0.15 m

Length = 1.8 m

Volume = 0.127 m^3

(Note that only the cylindrical part was taken into account after considering the irradiation areas of the vessel. The rest of the calculation is also for estimation purposes only)

If the processing flow rate is 400 Nm^3/hr, the retention time t_r is:

$$t_r = \frac{0.127}{400} \times 3600 \text{ secs}$$

$$= 1.14 \text{ sec}$$

Therefore, the estimated received dose for beam current at 2 mA is:

$$\text{Dose} = 111.96 \times \frac{1.14}{90} = 1.418 \text{ kGy}$$

3.4 Determination of flue gas humidity and temperature

The humidity was measured by passing a measured volume of flue gas through tared tubes containing granular anhydrous calcium chloride as desiccant. The apparatus used is as shown in Figure 3.3.

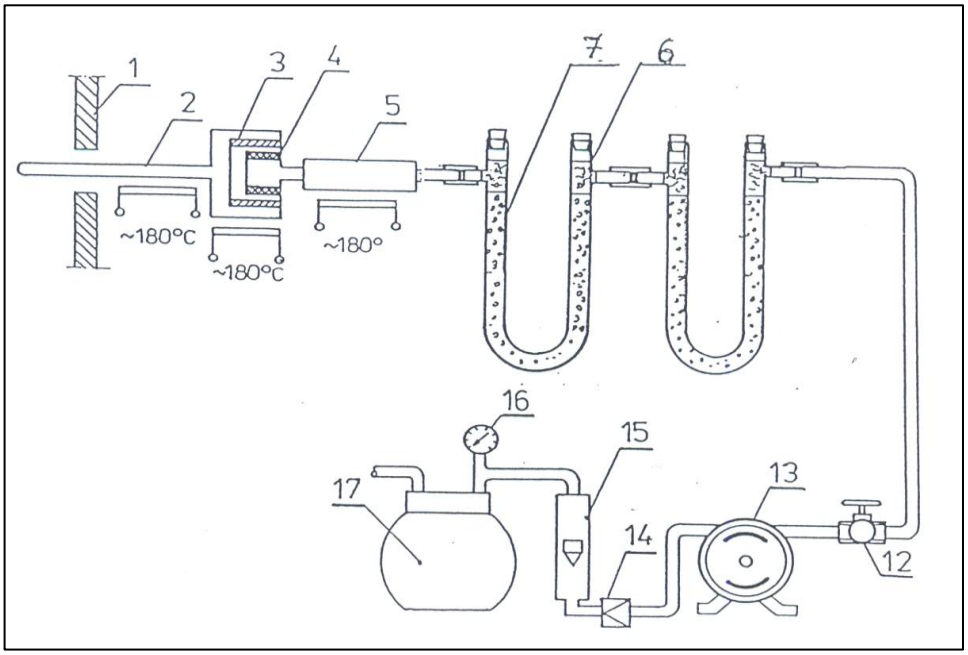


Figure. 3.3. H_2O sampling train

1. stack wall 2. heated gas sampling probe 3. inlet ceramic filter 4. outlet ceramic filter 5. heated sampling line 6. quartz wool 7. U-tubes filled with the granular $CaCl_2$ 12. needle valve 13. diaphragm 14. surge tank 15. flow meter 16. Thermometer 17.- gas meter

The increase in mass of the tubes was used to calculate the humidity as follows:

Mass of water stopped in two tubes

$$m = m_2 - m_1$$

Volume of sample gas at standard condition (0 °C, 101.32 kPa)

$$V_{gN} = V_g \bullet \frac{(P_{atm} + P_1) \bullet 273.16}{(t_g + 273.16) \bullet 101.32}$$

Where

V_{gN}:	volume of sample gas standard condition (NI)
V_g:	volume of gas measured by gas meter(I)
t_g:	average gas temperature, measured at gas meter (°C)
P_{atm}:	atmospheric pressure (kPa)/ [mmHg]
P_1:	average gauge pressure at gas meter (kPa)/ [mmHg]
273.16	absolute temperature equivalent to 0°C
101.32	pressure corresponding to 1 atmospheric pressure in kPa (replace with 760 if using mmHg)

The humidity (h) of flue gas is calculated from formula:

$$h = \frac{m}{0.001 \bullet V_{gN}} [\, g/N_m{}^3 \,]$$

When the humidity (h) should be expressed in percent by volume;

$$h = \frac{m}{0.001 \bullet V_{gN}} \bullet 0.12215 \; [\, \% \, (V) \,]$$

The humidity of the flue gas and temperatures at specified location were measured. The temperatures were measured using thermocouple placed that the selected locations. The humidity and temperature are very important parameters to ensure optimum output from the system. A spray cooler system was designed to increase the humidity of the gas while lowering the flue gas temperature. Apparently, the temperature of the gases had dropped much more than anticipated. According to Chmielewsky (1997) the desired humidity and temperature were between 12 – 14%v/v and 70 -75°C respectively.

The temperature dropped along the steel pipeline which was not sufficiently insulated. At the same time the desired humidity was not achieved. It was decided that new humidification system should be added to the test rig to improve the humidity and increase the temperature of the flue gases. The flue gas still needs to pass through the spray cooler since there was no other alternative route. The water spray was turned ON and/or OFF whichever is required.

A small steam generator capable of producing approximately 1.0 kg/hr steam was used for this purpose. The steamer's outlet was fixed to the inlet of the spray cooler. With the new humidification system set up, the humidity was maintained at an average value of 5.5% at the middle of the process vessel where the reaction mostly occurred. Although this is not enough to meet the optimum condition, it has proven that addition of steam to the system improved the humidity and increased the temperature of the flue gas. The experimental results obtained from using this humidification method had justified the need to get a

bigger steam generator at the later stage. The summary of humidity and temperature measurement is presented in the Table 3.3.

Table 3.3: Summary of Humidity and Temperature Measurement

Method of gas humidification	*Without dry gas*	*Without dry gas*	*Without dry gas*	*Right sprinkler*	*Left Sprinkler*	*Water vapor at outlet of the gas mixer*	*Water vapor with left sprinkler*
Sampling location	Inlet of the gas mixer	Inlet of the gas mixer	Middle PV	Middle PV	Middle PV	Middle PV	Middle PV
Humidity of flue gas % (v/v)	5.28	5.75	4.01	4.46	4.91	5.33	5.82
Gas flow m^3/h	140	155	160	190	190	150	260
Flue Gas Temperature (°C)							
Inlet TR, T1	78	85	82	88	102	76	103
Inlet SC, T2	68	76	72	76	89	69	90
Outlet SC, T3	50	56	54	35	36	50	39
Inlet PV, T4	46	51	50	38	37	46	43
Middle PV, T6	42	45	45	39	38	42	45
Outlet PV, T7	43	46	46	39	38	44	46
Inlet BF, T8	40	43	45	39	38	41	46
Outlet BF, T9	36	36	39	37	36	36	42

* TR – test rig SC – Spray cooler PV – Process vessel BF – Bag Filter

3.5 Method of Gas Analysis

It should be noted that the gas analysis methods and equipment used in this part of experiments were also used for the DBD experiments.

3.5.1 NO/ NO_x measurement

The flue gas analysis was done using an NO_x analyzer made by Thermo Environmental Industries, model no. 42C. The Model 42C is based on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. Infrared light emission results when electronically excited NO_2 molecules decay to lower energy states. Specifically, The Thermo Environmental Instruments, Inc. Model 42C is designated by the United States Environmental Protection Agency (USEPA) as a Reference Method for the measurement of ambient concentrations of nitrogen dioxide pursuant with the requirements defined in the Code of Federal Regulations, Title 40, Part 53.

Designated Reference Method Number: RFNA-1289-074

EPA Designation Date: December 11, 1989

For the EBFG experiments the gas was sampled by a dilution probes located at the inlet of the spray cooler (CEM1) and outlet of the process vessel (CEM2), (refer to Figure. 3.1)

The NO was measured directly by the instrument together with the total NO_x. The amount of NO_2 was calculated internally by using a simple calculation based on the equation:

$$\text{Total } NO_x = NO + NO_2$$

3.5.2 SO_2 measurement

The SO_2 was measured directly using the Thermo Environmental Industries SO_2 analyzer, model number 43C. The Model 43C is based on the principle that SO_2 molecules absorb ultraviolet (UV) light and become excited at one wavelength, then decay to a lower energy state emitting UV light at a different wavelength. Specifically, the Thermo Environmental Instruments, Inc. Model 43C is designated by the United States Environmental Protection Agency (USEPA) as an Equivalent Method for the measurement of ambient concentrations of SO_2 pursuant with the requirements defined in the Code of Federal Regulations, Title 40, Part 53.

Designated Equivalent Method Number: EQSA-0486-060

It should be noted that the SO_x analyzer had suffered several damages during the course of experiments that most of the times the readings were unreliable. Since these studies were focused on NO_x, quantification of SO_x was not determined unless needed. In this case, estimation of SO_x was made by measuring the acidity of the exit gas. This method was only use for the DBD experiments since the flow rate was low and manageable.

3.5.3 Calibration of analyzing instruments.

Calibrations of both analyzers were carried out using standard gases supplied by Linde Gas. The standard gas was a mixture of SO_2, NO and N_2 as balance. The concentration of each gas varies in every cylinder used as stated in the accompanying certificates.

The initial calibration was done using the gas calibrator, Dynamic Gas Calibrator, Thermo Environmental Industries, model no.146C. However, when at site, i.e. at the Plasma Lab, direct calibration method was applied. In this case, the standard gas was fed directly into the sampling chamber, and the calibration factors were noted.

3.6 Component test

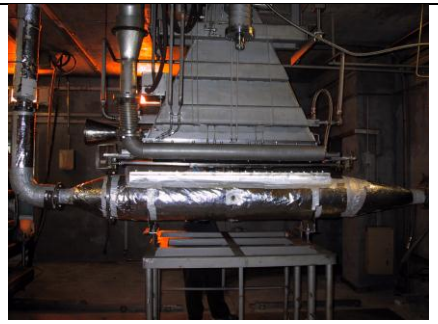
Tests were carried out on individual major components prior to actual running of the experiment to ensure that they are functioning. The test results, as well as the function of each component, are described in Table 3.4. It was also important to carry out leak test

along the pipeline to avoid unnecessary emission of flue gas in the working area. In obvious cases, the leakage can be detected by observation and smelling. Simple soap and water test was used to trace leakages in more subtle areas such as at the joints and connections to the probes. Tar like cement was used to seal big leakages and silicon glue for smaller and discrete leakages.

Table 3.4: Summary of component test

Components	**Function**	**Test result**	**Photo**
1. Generator sets (2 units)	To provide continuous flue gas to the system	Flow (per unit) occasionally varies from 120 to 250 Nm^3/h	
2. Static mixer	Natural gas mixing method	No test necessary	
3. Spray cooler	To reduce gas temperature to the required process value	Measured temperature at process vessel ranges between 30° to 40° C	

4. Continuous Emission Monitoring System (gas analyzers)	To measure individual flue gas components	Functioning and calibrated	
SOx analyzer (inlet)	To measure SO_2 at inlet point	Functioning. Calibrated against standard gas	
SOx analyzer (outlet)	To measure SO_2 at outlet point	Functioning Calibrated against standard gas	
NO_x analyzer (inlet)	To measure NO, NO_2 and total NO_x at inlet point	Functioning Calibrated against standard gas	
NO_x analyzer (outlet)	To measure NO, NO_2 and total NO_x at outlet point	Functioning Calibrated against standard gas	

NH_3 analyzer	To measure NH_3 at outlet, before emission to the stack	Functioning and calibrated against standard gas	
O_2 analyzer	To measure oxygen content in FG at inlet	Functioning	
Zero air supply	To supply zero air for CEM	Functioning	
Gas calibrator	To calibrate individual analyzers	Functioning	
4. Process vessel	To provide process area in the irradiation room	Possible leakage at flange joints due to frequent disassembling	

5. Dust collector	To collect and filter the by-product from the treated air	Functioning	
6. Flow meter	To measure flow of flue gas at inlet	Functioning	
7. Thermocouples (x9)	To measure temperatures at identified location	Functioning but not calibrated.	

3.7 System test without electron beam bombardment.

After the tests on the major components had been completed, the test rig was ready to run as a system. Initial runs were made without turning on the electron beam machines. Several measurements were made to determine the values of the gas components, namely SO_2 and NO_x. The average values of SO_2 and NO_x at different flow rates were recorded in the Table 3.5 below. The flow rate was varied by increasing or decreasing the speed of the generator. Higher speed will produce higher flow rate. The table shows that the concentration of the pollutants increased with the flow rate. This behaviour represented the condition of this particular generator/ engine only.

Table 3.5: Concentration of flue gas components at different flow rates.

Flow rate Nm^3/h	**SO_2 (ppm)**	NO_x **(ppm)**
120	6.5	108
150	7.5	155
200	10	160

Usually, as the engine speed drops, the gas temperature inside the cylinder tends to rise, and the residence time of combustion gas increases under high ambient temperature. Therefore, the concentration of NO_x formed in the emission gas increases as the speed drops. This was shown by a simulation carried out by Nagai (1991) where the quantity of NO formation was determined from the calculated temperature, cylinder pressure, the chemical equilibrium compositions of N_2, NO, O_2 and OH. Nagai (1991) had also shown that NO_x would increase if the load on the engine increases.

The generator set used in this study was an old, inefficient engine that had served Tenaga Nasional for years to provide electricity in villages. Being an old engine, it was expected that the combustion performance will not be ideal and that the load on the engine would be high. Therefore, the results obtained in these measurements were justified although not following the ideal condition.

3.8 Experimental Procedures

3.8.1 Preparation

In general, all equipment is needed to be warmed up as specified by the respective manuals. There are two sections that needed to be operated during the experiments namely the test rig and the EB machine. Only trained and licensed personnel can operate the machine. All information regarding the required EB parameters (energy, beam current and dose) were conveyed to the operator in advance. The generator set was started and left to run until the reading on the analyzers were approximately consistent. This also allowed time for the analyzers to warm up.

3.8.2 Irradiation time

The irradiation will start when it was satisfied that the flue gases emitted from the diesel engine were consistent. The irradiation time will vary depending on the real time data observed on the analyzers.

The variable process parameter was the beam current. The flue gas flow was maintained at the required rate which is normally around 150 – 200 Nm^3/h. The accelerator voltage was kept at 1MeV to minimize the total power consumption. During the experiment, the beam current can be varied from 1 up to 30 mA. However, since it is necessary to keep the total power as low as possible then, the maximum beam current was targeted at 15mA. The data was recorded in real time via the TEI software and converted into graphical form using Microsoft Excel.

3.8.3 Radiation safety

Only qualified and certified operator can operate the EB machine. The experiments can only be done after approval of the facility's authority. All radiation safety precautions were observed as required. This includes working only in areas that have been designated as clean area and wearing the film badge while in the area.

It should be noted that although electron beam has limited penetration power as it hit metal or other heavy elements, x-ray radiation can be formed. This phenomenon is called the bremsstrahlung effect. Hence, the radiation safety refers to protection against beta radiation (electron beam) and x-rays.

CHAPTER 4:

METHODOLOGY PART 2:
DIELECTRIC BARRIER DISCHARGE

This chapter describes the experimental setup of the second method used in this study to remove nitric oxides in gas stream. The reactor was developed by the Plasma Technology Research Centre at the University of Malaya, Kuala Lumpur. Initially, it was used to convert oxygen, either as pure gas or component of air fed into the system, into ozone for various applications. In this study, the gas stream containing pollutants was fed into the system as the inlet gas and reacted with the energetic electron stream inside the DBD tubes before exiting through the outlet point. This resembled the process of electron beam flue gas treatment as previously described.

This chapter also details the features of the DBD reactor by looking at the design, discharge properties and images of the filamentary discharges. The experimental procedures are laid out together with the general safety and operational precautions.

4.1 Dielectric barrier discharge tube

The most important feature of dielectric barrier discharge is that the non-equilibrium plasma can be achieved at atmospheric condition. The DBD configuration with respect to the geometrical shape, operating parameter and medium is flexible. In this study, a coaxial configuration as in Figure 4.1 was chosen.

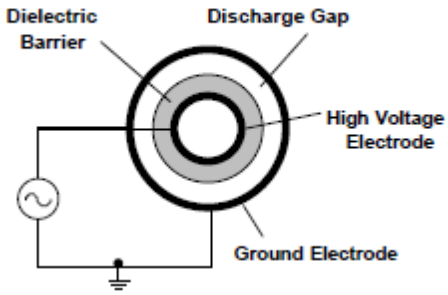


Figure 4.1: Coaxial DBD tube configuration.

Each DBD tube is made up of two cylindrical electrodes, with a dielectric material placed in between them. The inner electrode is made of hollow stainless steel rod with outer diameter (OD) of 16 mm. One end of the electrode is connected to the high voltage terminal. A standard 20 mm OD Pyrex glass test tube is used as the dielectric. The test tube is placed over the other end of the inner electrode, creating a dielectric barrier between the inner and the outer electrodes. The outer electrode is a hollow stainless steel cylinder with OD of 30 mm. When these components are assembled, a gap of approximately 4 mm between the glass and the outer electrode is created for the gas to flow. The gaseous chemical reaction occurs within this narrow gap where the discharge is formed along the length of the glass tube.

The inlet and outlet points are also built on the outer electrode. The DBD tube is powered by an AC power supply that can generate up to 40 kV peak to peak voltages. The high voltage power supply will be discussed later in this chapter. The parts are assembled on an insulator base at the HV terminal point. The schematic diagram is as shown in the Figure 4.2.

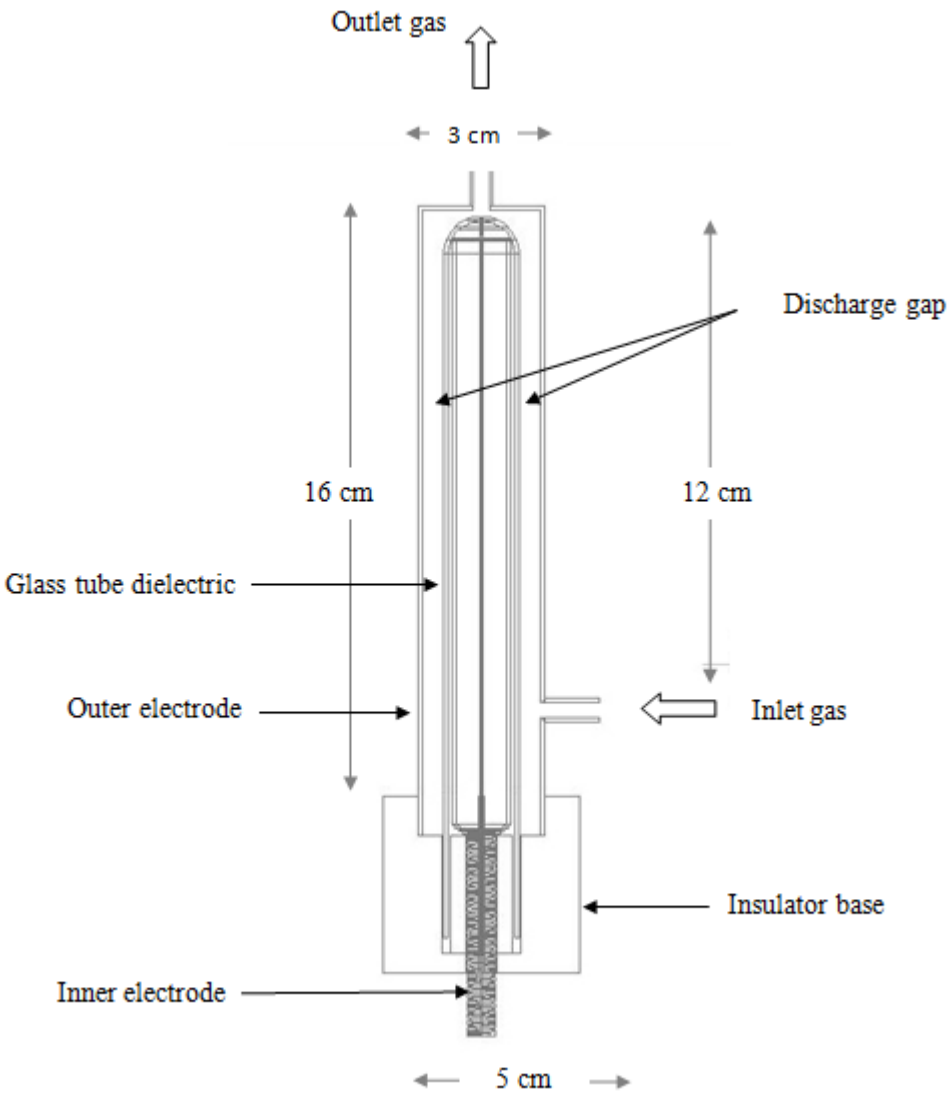


Figure 4.2: Schematic diagram of a single DBD tube.

The geometrical dimensions of the tube are described below and are used to calculate the processing volume. The processing retention time is derived from the flow rate and volume.

Outer electrode:

Dimension:

Length	=	160 mm
OD	=	30 mm
ID	=	28 mm (wall thickness = 1 mm)
Radius, r	=	14 mm
Inner volume	=	$\pi r^2 \times h$
	=	$3.14 \times (1.4)^2 \times 16$
	=	98.47 cm^3

Test tube (dielectric) : [gap size ≅ 4 mm]

Dimension:

Length	=	180 mm
Effective length	=	150 mm
O/D	=	20 mm
Volume	=	$3.14 \times (1.0)^2 \times 15$
(Assumed cylindrical)	=	47.1 cm^2

Effective processing volume	=	98.47 - 47.1
	=	51.4 cm^3
		(approximately 50 cm^3 or 0.05 liter)

For gas flow rate of 5 scfh (2.36 lpm),

=> processing time (retention time in each tube) $= \frac{0.05}{2.36}$ x 60 s

$= 1.27$ s

(Note that for the purposes of estimation, the calculations made were based on assumptions that the processing area is cylindrical).

4.2 The dielectric barrier discharge reactor

The DBD tubes are assembled and connected to the high voltage power supply to make a table top reactor for the experiments. Teflon tubing is used to connect the reactor to the feed gas tank and to the outlet point. Since the reactor is of table top size and also portable, more experiments can be carried out by manipulating several aspects of the system such as flow rate, voltage, number of tubes and configuration or arrangement of the tubes. The general schematic diagram of the experimental setup is as shown in Figure 4.3 below:

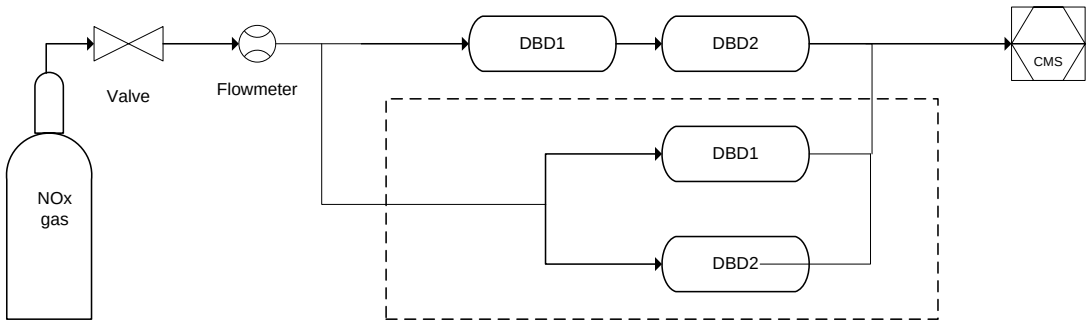
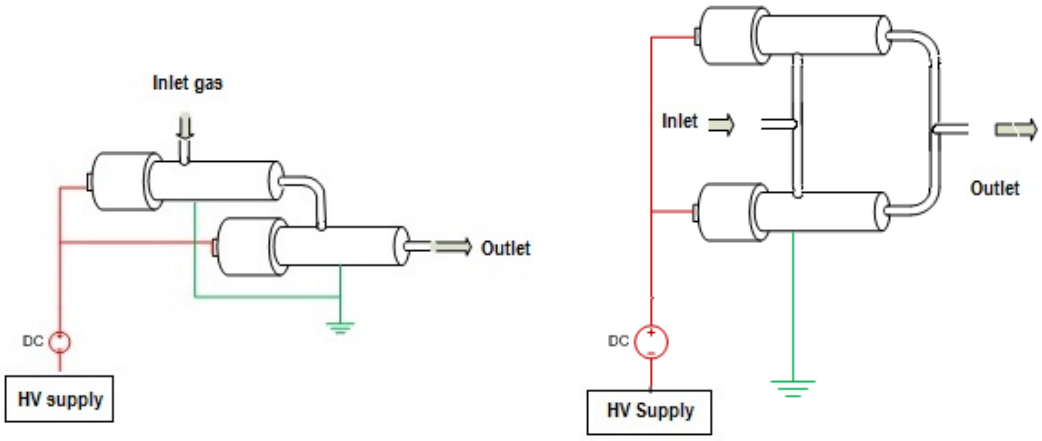


Figure 4.3: Schematic diagram for NO_x removal experimental setup. The DBD units are connected either in series or in parallel (as shown in dotted-line box).

The reactor is a modular type such that the number of tubes can be added or removed easily. The tubes can be connected either in series or in parallel with respect to the gas flow as shown in Figure 4.4. Electrically, however, whichever way the tubes are configured, the electrical connection is still in parallel. This means that as the number of tubes is increased, the current flow into each tube will be reduced while the voltage will not be affected. Each tube can be represented as a capacitor as illustrated in Figure 4.5.



(a) (b)

Figure 4.4: Schematic diagram of DBD tubes connections (a) in series and (b) in parallel. The electrical connection remains the same (parallel).

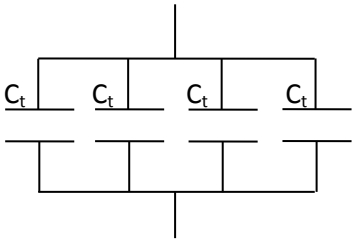


Figure 4.5: Schematics of capacitors representing four DBD tubes connected in parallel.

If the capacitance of each tube is C_t then:

$$C_{total} = C_t + C_t + C_t + C_t$$

$C_{total} = NC_t$

Where N = number of the tubes

Hence, electrically, the number of tubes in parallel connection will increase the capacitance and reduce the reactance across the tube.

$$Z_c = \frac{1}{\omega C_{total}}$$

Increasing the number of tubes will affect the current flow in each tube and hence the overall efficiency of the reactor.

The other auxiliary components to complete the reactor are the feeding gas line and flow meter. The feed gases for the experiments were specially mixed for the purpose. There were three different mixtures used:

51.2 ppm NO, 30 ppm SO_2, balanced with N_2
100 ppm NO balanced with N_2
106 ppm NO, 300 ppm SO_2 balanced with N_2

The values given are in ppm referring to the part per million in terms of mole, as stated in the certificate of analysis provided by the supplier. Since the manufacturer certified the concentrations of the mixtures, the gases were also used to calibrate the analyzers. The experiments were carried out in phases and in each phase different gas mixture was used.

A flow meter was used to control the input flow rate. The scale on the flow meter was in *standard cubic feet per hour* (scfh*)* with flow rate range 0-5 scfh. A higher range 0-50 scfh was also used in certain parts of the experiments.

A chemiluminescence's type NO analyzer (TEI Corporation, model 42C) was used to analyze the output continuously throughout the process. This method of analysis was the same as previously used in the electron beam test rig described in Chapter 3.

4.3 High voltage power supply

The AC high voltage power supply provided sinusoidal output at 50 Hz frequency. The basic circuit diagram for this power supply is as shown in Figure 4.6. The voltage measurement was done by setting up the voltage probe (Tetronix P6015) as shown in Figure 4.7. The waveform was observed and readings recorded by an oscilloscope (Tetronix TDS 2024). The basic power supply was used in the preliminary experiments. Later it was modified where four more capacitors were added to the original circuit. With the additional capacitors, the amplitude of the output voltage is higher and more stable (Figure 4.8).

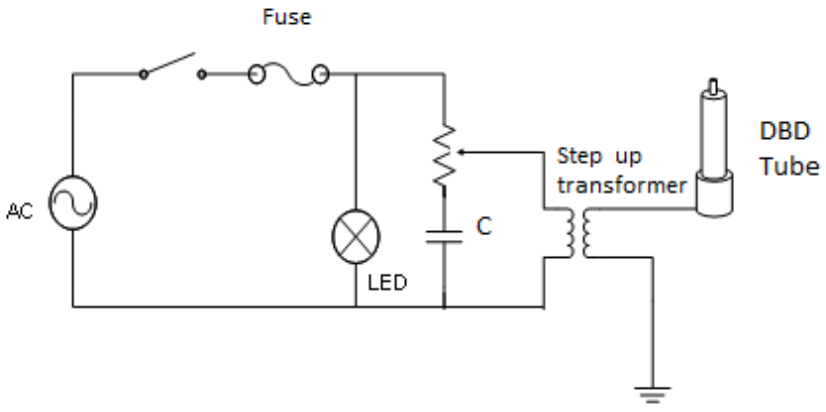


Figure 4.6: The basic circuit diagram for the original HV power supply.

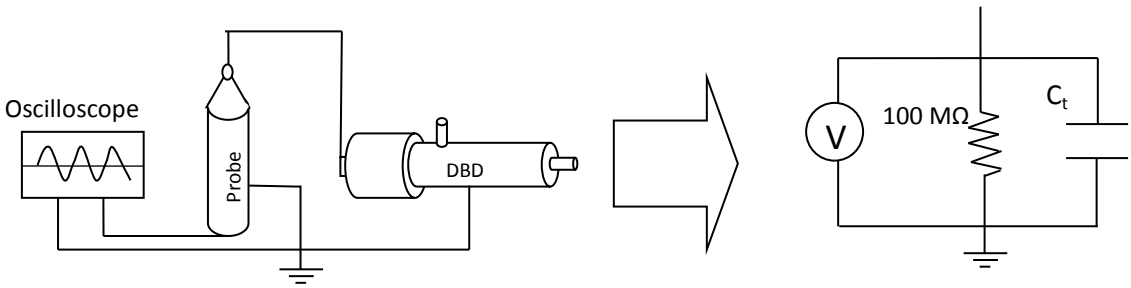


Figure 4.7: Setup for voltage measurement.

Table 4.1: Measured voltage from the basic HV power supply.

Dial #	0	1	2	3	4	5	6	7	8
Voltage (p-p)	28.2	28.0	26.8	25.4	24.4	22.8	19.8	15.8	7.5

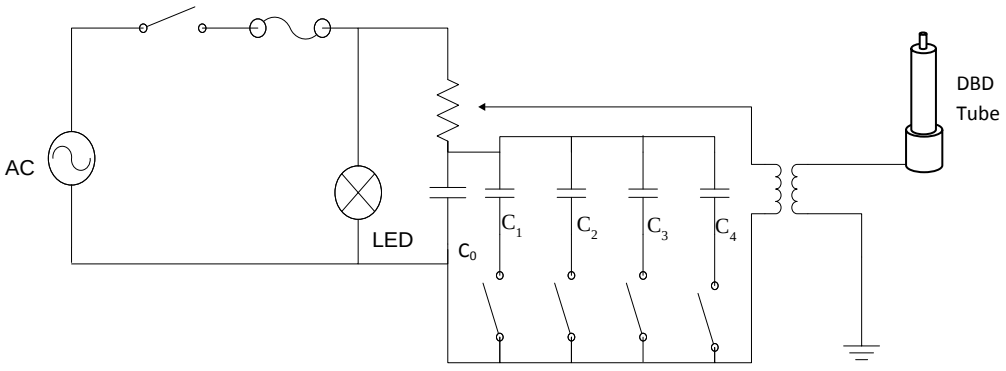


Figure 4.8: The modified HV power supply.

Table 4.2: Measured peak to peak voltage (in kV) for various combinations of dial switch and number of capacitors.

Dial #	**C0**	**C1**	**C2**	**C3**	**C4**
0	28.2	31.3	34.4	38.2	42
1	28	31.0	34.4	38.2	42
2	26.8	31.1	33.2	36.6	40.2
3	25.4	30.7	32.4	34.8	38.2
4	24.4	30.4	31.4	32.2	35
5	22.8	22.8	29.6	31	31.4
6	19.8	22.5	29.6	27.4	29.8
7	15.8	17.0	21.1	24.2	23
8	7.5	11.4	12.4	13	13.6

The waveforms in Figure 4.9 and 4.10 display the waveform of a 50Hz signals with periodic time of 0.02s. While the voltage appears as sinusoidal waveform, the current appears as burst of sharp pulses with random amplitudes. These current bursts are formed at every half cycle of the applied voltage and they correspond to electron streams that provide energy to induce the chemical reaction in the gas being treated. The figures also show that at 31 kV the burst contained current pulses with higher amplitudes compared to 27 kV. It is expected that more chemical reaction can be generated by these pulses.

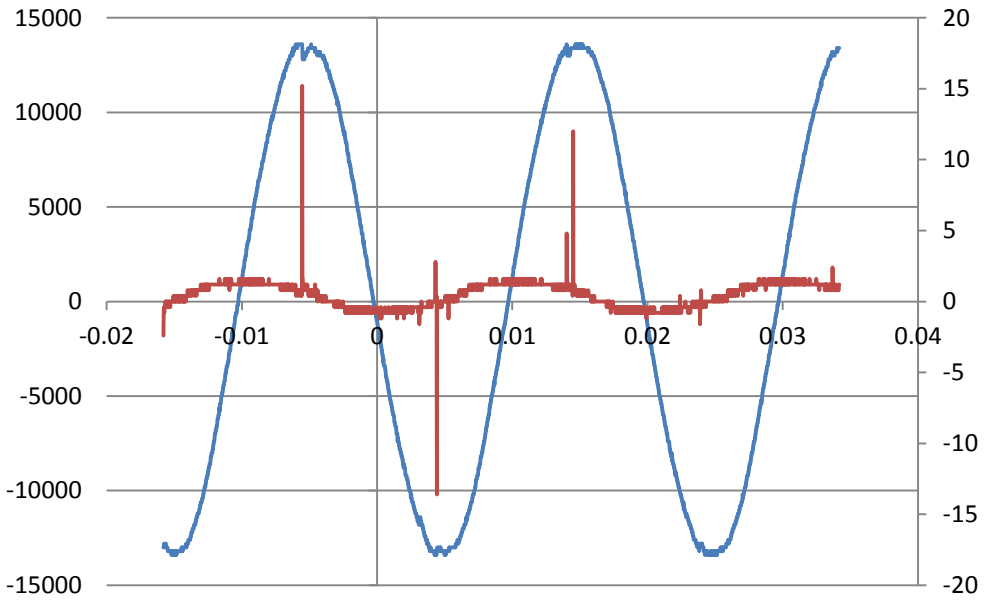


Figure 4.9: Waveform at voltage 25 kV pk-pk.

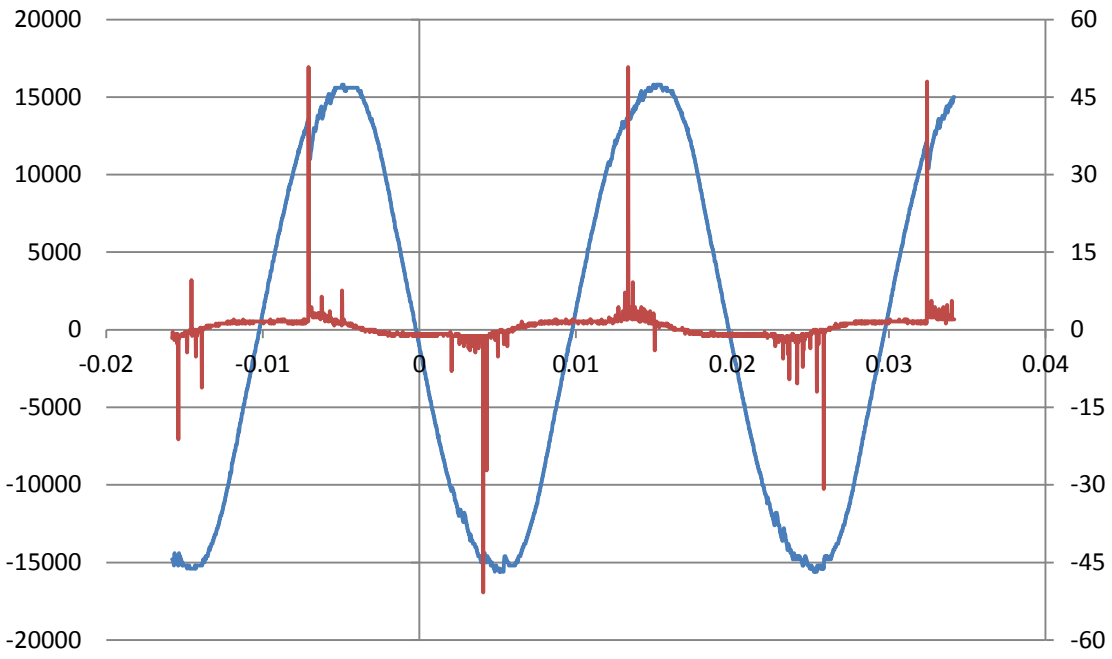


Figure 4.10: Waveform at voltage 31 kV pk-pk.

4.4 Photographic imaging of the DBD discharges

Dielectric barrier discharge can occur in the form of 'filament' or 'diffuse discharge' depending on the environment it is produced. In this study, filamentary dielectric barrier discharge is anticipated. The filamentary mode can be obtained in atmospheric pressure where tiny current channels occurred across a gap between two insulated electrodes, as in the DBD tube being used. These micro discharge filaments can be characterized as weakly ionized gases with properties resembling those of transient high-pressure glow discharge (Kogelschatz 2000).

A special tube was constructed to enable us capture the image of the micro discharges. This tube has the same feature as the original tube except the top was covered with glass (Figure 4.11). The images were taken with a Nikon camera with automatically adjusted exposure time. This part of work was assisted by a graduate student, Mr. Tay Wee Horng. This work was done to demonstrate the discharge filaments and how it behaves with change of applied voltage.

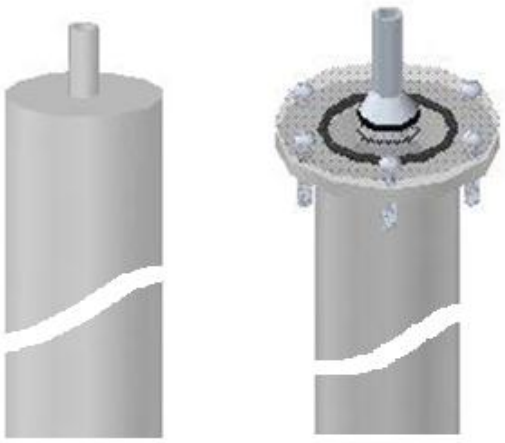
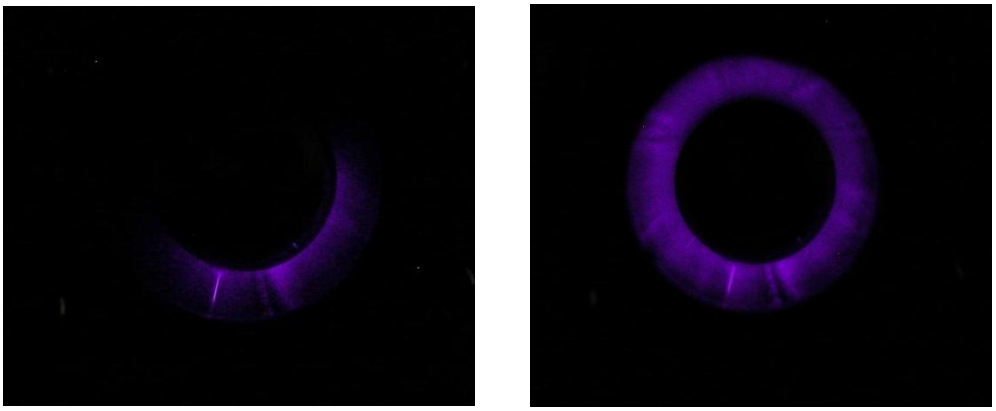


Figure 4.11: Special tube constructed to enable photographic imaging.

Figures 4.12(a) and 4.12(b) show the images of the discharges at different voltages. At 25 kV, the discharges were not well distributed around the dielectric (Fig 4.12a). The filamentary nature of the discharges can also be observed quite clearly.



(a) (b)

Figure. 4.12: (a) Discharge images at voltage of 25 kV, and (b) at voltage of 30 kV.

At 30 kV, the image obtained shows that the distribution of the filaments is more regular and even around the dielectric. This means that as the external voltage was rising, additional microdischarges were initiated at new locations because the presence of residual charges on the dielectric has reduced the electric fields at positions where microdischarges had occurred. When the voltage was reversed, the next microdischarge will form at old microdischarge location. According to Kogelschatz (2000), high voltage low frequency operation tends to spread the microdischarge, while low voltage high frequency operation tends to reignite the old microdischarges channels every half

period. This is common dominant feature in all dielectric barrier discharge which is called the memory effect caused by charge accumulation on the dielectric.

The images also explain why low efficiency was achieved during the preliminary experiments where the maximum available voltage was only 28 kV. The intensity of microdischarges occurred was much less than when the voltage was higher.

4.5 General experimental procedure

The following are the step by step general procedures for the gas treatment experiments:

a. The analyzers are first on and allowed to warm up.
b. Set the DBD's operating voltage as required.
c. Open the gas regulator and allow the gas to flow, at the lowest flow rate possible, through the system and the analyzer, until the reading on the analyzer stabilizes.
d. Slowly regulate the flow meter to set at the required flow rate.
e. Allow at least a minute before turning on the DBD reactor's power supply
f. Run the experiment for the required period.
g. At the end of the experiments, save the data recorded by the TEI software.

The experiments were carried out in three phases as described as follows:

A. Phase 1 experiments – Preliminary works

The main objective of this experimental stage was to investigate the possibility of using the reactor to remove NO from the gas flow and also the factors that are affecting the removal rate. At this point, the original power supply and tubes were used. The feed gas was a mixture of NO (51.2 ppm), SO_2 (30 ppm) and N_2 (balance), where the variables were the flow rate, voltage and tubes configuration (parallel or serial).

B. Phase 2 experiments

The main objective was to investigate further the factors that are affecting the removal rate. The experimental conditions were based on the gas compositions as below:

Condition A. Nitric Oxide (100 ppm) and nitrogen only (as balance gas)

Condition B. Nitric Oxide (100 ppm) + Sulfur dioxide (300 ppm) and nitrogen gas (as balance)

Condition C. Nitric Oxide (100 ppm) + Sulfur dioxide (300 ppm) + nitrogen gas (as balance) and added external air.

C. Phase 3 experiments

In this phase of experiments, the basic experimental parameters should have been established. The optimization will be done by exploiting the number of tubes and manipulating their connections. The feeding gas used will be that of Condition C.

It should be noted that the feed gas in condition A is the nearest to the diesel emission since it does not contain SO_2. However, real diesel emission will also contain other elements such hydrocarbons, carbon dioxide and other volatile organic compound which difficult to simulate. The experiments were carried out to find out if the DBD can effectively clean gases contaminated with high concentration of NO. The different backgrounds gases are added to see if the efficiency are affected by the other pollutants, mainly SO_2. The gas composition B and C has the NO to SO_2 ratio (1:3) which is the nearest equivalent to coal fired flue gas (ratio of 1:2) as earlier seen in Table 1.5.

4.6 General precautions

The experiments must be done in the designated area where proper ventilation and air suction systems were installed. All ventilation and air suction systems must be turned on prior to start of an experiment. This is to ensure that the gases will not flow to outside the experimental area. A two valves stainless steel special gas regulator was used to regulate the gas flow into the gas line. Teflon tubing was used throughout the gas line.

a. Leak test on gas line and tubes

Leak tests were carried out prior to running any experiments. A simple soapy water and sponge were used to test any leakage around the reactor gas line. During the test, only air was used to flow into the reactor. The same type of test was used to check the individual tubes. Any leakages on the connectors and joints were tightened and sealed using silicon sealant or glue. Leaked tubings were simply replaced with new ones.

b. Electrical safety

Since the experiments involve high voltage, precaution must be taken to prevent electric shocks. The reactor must be properly earthed, and rubber-soled shoes were worn during operation. Hands must be free of any metallic ornaments such as gold bangles or ring since the discharge may jump to these objects.

CHAPTER 5

REMEDIATION OF FLUE GAS FROM DIESEL EMISSION USING ELECTRON BEAM

This chapter presents the results obtained from all experiments using the electron beam flue gas treatment test rig. Initially, the system was tested with electron beam using the estimated parameters derived from the design values. Results from the preliminary tests were used to optimize the test rig.

5.1 System test with electron beam

The full system test with electron beam started after completing full inspection throughout the test rig. It was crucial to ensure that there were no leakages along the pipelines since the gases in the system were toxic in nature.

In order to choose the starting parameters for the electron beam machine, several assumptions were made:

- The flue gas flow rate was at 200 Nm^3/h.
- The electron beam energy remained at 1 MeV for all experiments
- Working or processing dose was 10 kGy, based on works such as those reported by Chmielewski (1995), Basfar (2008) and reports from the IAEA (IAEA TecDoc 1023).
- The beam current was calculated using the dosimetry results as previously mentioned in Chapter 3 and, as follows:

  At 1 MeV, 2 mA, the dose was 111.96 ± 28.97 kGy per 90 s
  (*as issued by the SSDL)

Estimated dose rate	=	1.24 kGy per s
Volume of PVy,	=	0.127 m^3
Flow rate	=	200 Nm^3/hr
Retention time t_r	=	$\frac{0.127}{200} \times 3600$ s
	≈	2.3 s
Actual dose	=	Dose rate x retention time
	=	1.24×2.3
	=	2.85 kGy (beam current 2 mA)

As the dose increases linearly with beam current, therefore, the estimated beam current to produce 10 kGy:

Beam current = $\frac{10\ kGy}{2.85\ kGy} \times 2$ mA

= 7.0 mA

The preliminary experiments were carried out using these basic parameters where it was estimated and assumed that the flue gases would receive 10 kGy as it passed through the process vessel for the stipulated time. It should be noted that the absorbed dose or dose received by the gas particles is directly proportional to the exposure time. The longer the retention time, the higher the dose will be. This also means that the actual dose would vary if the gas flow is inconsistent due to the inefficiency of the generator set.

5.2 Preliminary results

The first observation made during the experiment was that the concentration of NO reduced significantly with the exposure of electron beam in the process vessel. The accelerated electrons were released as soon as the shutter of the window opened. A typical chart recording the real-time changes in concentration of NO_x during the irradiation is as shown in Fig 5.1. The chart shows how NO, NO_2 and hence the total NO_x vary along the time axis as the electron beam machine was turned ON and OFF. In this particular case, the experiments were carried out in a dry environment, without additional moisture. The spray cooler was turned off. The concentration of NO decreased sharply, from 130 ppm to 25 ppm (~80% removal), and almost instantaneously as the beam shutter opened (beam ON), and the flue gas was exposed directly to the electron beam. This behaviour was also an important indicator to determine whether the EB machine was operating properly or not. For example, if there

was no change observed in the concentration of the NO, it might indicate that the window shutter had failed to open and hence the electron beam could not enter the process vessel.

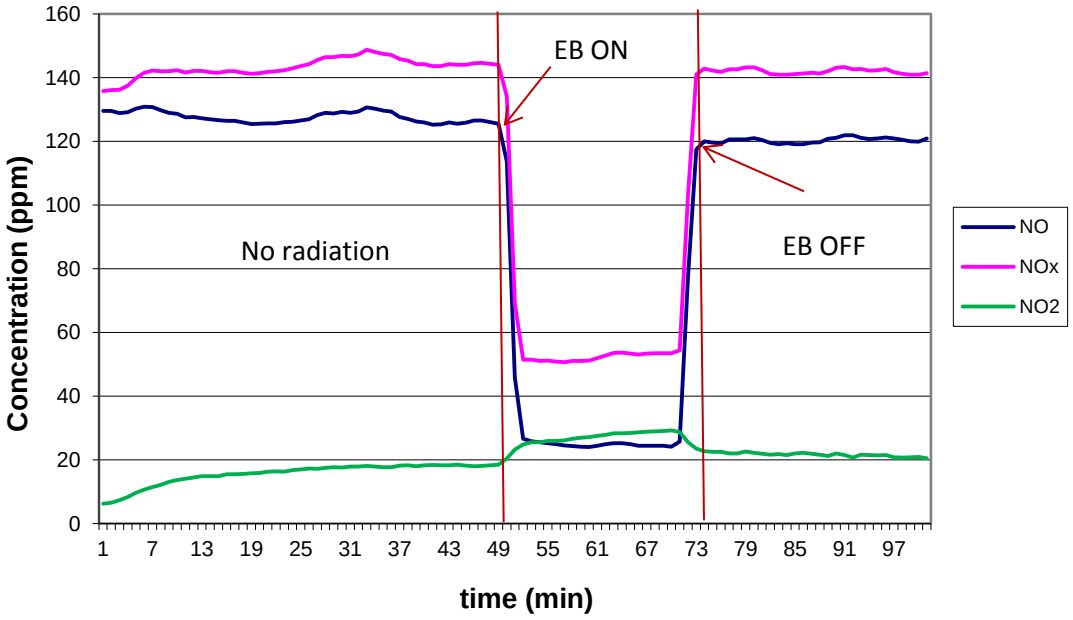


Figure 5.1: Typical NO, NO_2 and NO_x concentrations versus time chart.

As mentioned earlier in Chapter 3, the spray cooler in the original test rig design had caused drastic temperature drop without improving the moisture content or humidity. A small steam generator was added to improve the humidity and temperature. The next experiments were done by varying the humidification method. Figure 5.2 shows the changes in the concentration of the NO and NO_x as the flue gases being irradiated in different humidity conditions, along the time axis. The results were logged continuously in real-time, from the NO_x analyzer where the data were recorded at 1 minute interval.

The chart in Fig 5.2 is divided into four regions. Each region represents different experimental conditions as below:

Region A: without EB irradiation
Region B : With EB irradiation + steam
Region C : With EB irradiation + steam + spray cooler
Region D : With EB irradiation + spray cooler

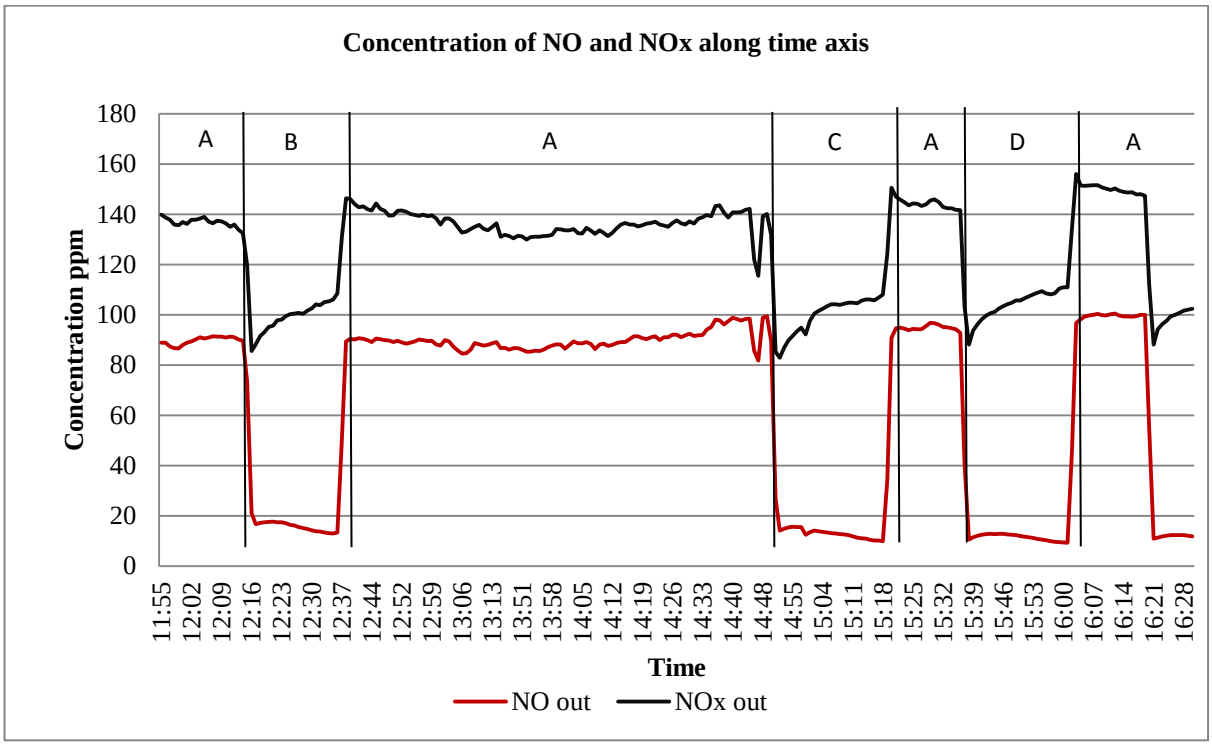


Figure 5.2: Removal efficiency of NO and NO_x in different humidification conditions.

In this chart, the initial concentration of NO and NO_x varies between 90 -100 ppm and 130 – 150 ppm respectively (regions A). As soon as the beam shutter opened, the concentrations went down quite drastically for NO, to around 10 – 18 ppm (~90% removal). However, for the total NO_x, the removal was low i.e. down to 90 – 110 ppm (~28% removal) (Region B). The main reason was the oxidation of NO which gave rise to the NO_2 and subsequently, the total NO_x.

With the addition of steam and water moisture from the spray cooler (region C), small changes were observed for NO_x removal (~40%) and insignificant improvement for NO removal. Using the spray cooler alone (region D) gave almost similar results as the previous condition (region B). The humidification was thought to be insufficient to make any significant improvement to the system.

5.3 Optimizing the flue gas treatment system test rig

Results obtained in the preliminary tests were reviewed to improve the test rig so that the outcome can be optimised. The most significant improvement that needed to be done was to increase the processing temperature and humidity. The preliminary test using a small steam injection had justified for installation of a bigger steam generator. Some insulation materials were wrapped around some parts of the pipeline to preserve some of the heat. With these improvements, the humidity and temperature of the flue gas had improved significantly. Table 5.1 shows the humidity measured for different conditions inside the process vessel where the reactions will occur.

Table 5.1: Humidity and temperature of Flue Gases.

Location of sampling	**Humidification method**	**Humidity % v/v**
inside Process Vessel	Dry	4.01
inside Process Vessel	with small steam generator	5.35 – 5.37
inside Process Vessel	With big steam generator	11.95 - 13.73

Location	Inlet of PV	inside PV 1	inside PV2	outlet PV
Temperature (°C)	62	62	61	64

With this improved condition, the next step was to run the experiments at different level of beam current (hence different radiation doses) to find the optimum parameter set up for the electron beam machine.

The advantage of using the EPS 3000 electron beam machine was that it could provide variable beam currents from 0 – 30 mA. However, since higher beam current would mean higher cost, the experiments were limited to use up to 15 mA only. Figure 5.3 shows the analyzed data based on real time, obtained during a single experiment for beam current varied from 0 – 10 mA. The beam current was increased by 1 mA at every 10 minutes interval. It can be seen the concentration of NO reduced as the beam current increased. A clear down step pattern was observed for beam currents values of 0, 1, 2 and 3 mA. The drop occurred almost immediately as the beam current changed. At mid-range (between 4 – 6 mA, corresponding to between 30 to 60 minutes along the time-axis) this changes became less obvious and in fact, the concentration tend to rise

than at previous current. This could be due to some experimental error such as unstable flow rate (from the generator) and hence different quality of feed gas. However, the overall results had shown that at higher than 7 mA, the NO concentration dropped again following the earlier pattern. The experiment was repeated 2 more times where the data for the different beam currents were logged for 10 minutes each time. The beam current was varied from 0 -12 mA to enable us see the effect on the removal rate at higher current. It should be noted that the irradiation time was limited by the demand from other users and thus the experiments cannot be repeated many more times.

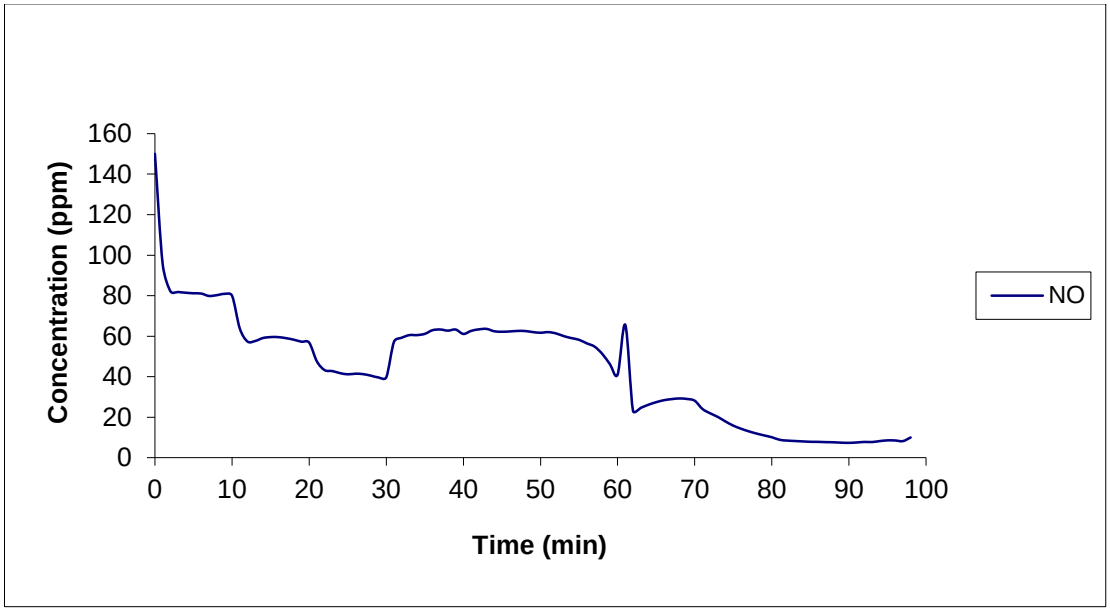


Figure 5.3: Concentration of NO against time of irradiation. Changes of beam current occurred every 10 minutes

It was then observed that the concentration of NO was almost consistent for each beam current. Hence, the averaged values were calculated based on the 10 minutes exposure and presented as shown in Figure 5.4. At this point, it was also important to observe the formation of NO_2 as a result of oxidation inside the vessel. This is shown in Fig. 5.5 where it can be seen that as NO decreased with beam current it was actually being oxidized into NO_2 as indicated from the increase of its concentration.

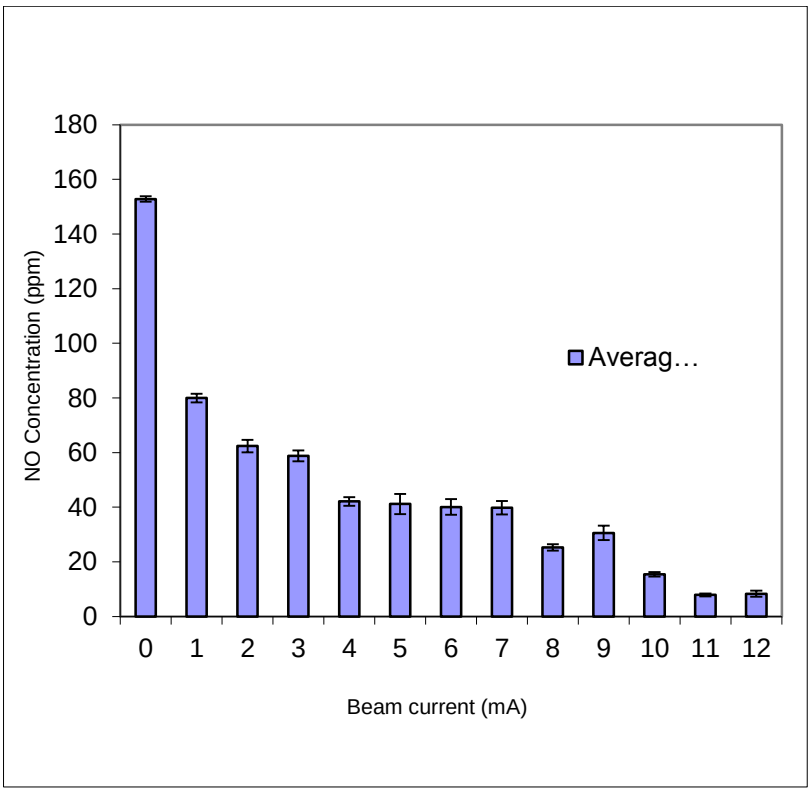


Figure 5.4: Average concentration of NO when bombarded with electron beam against different beam current.

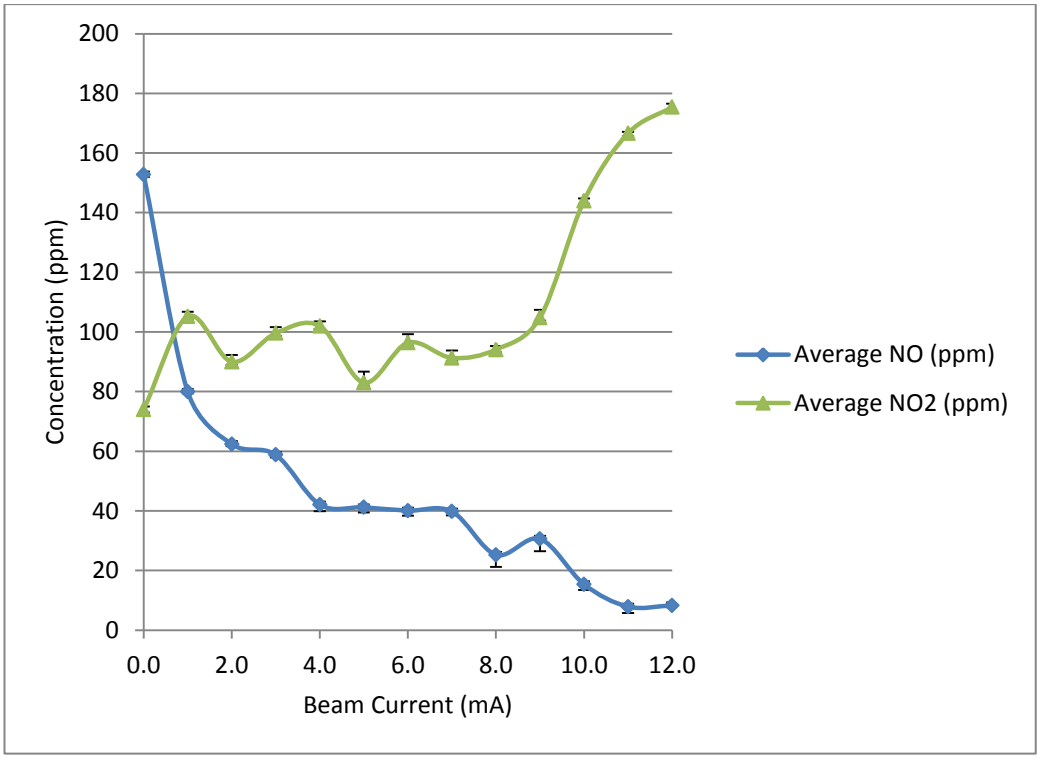


Figure 5.5: Average concentration of NO and NO_2 at different level of beam current.

Figure 5.6 presents the variation of calculated removal efficiency against electron beam current. As expected, higher current give higher efficiency. The polynomial of second order equation was added to show the trend of the removal efficiency with increasing beam current. The removal efficiency (%) was calculated using the formula:

$$\eta(\%) = \frac{[NO(in)] - [NO(out)]}{NO(in)} \times 100$$

This formula was also used to calculate the removal efficiency when using the dielectric barrier discharge system.

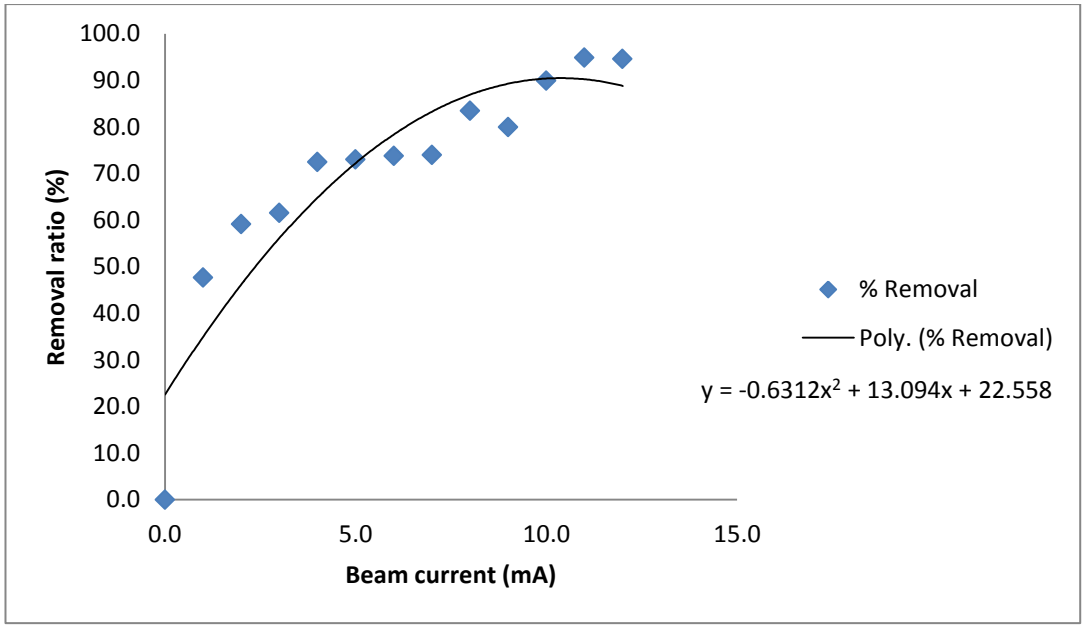


Figure 5.6: NO removal efficiency (%) for different beam current.

The optimum beam current was calculated using the derived polynomial equation, as below:

$$y = -0.6312x^2 + 13.094x + 22.558$$

$$\frac{dy}{dx} = (-1.2624\,x) + 13.094$$

Hence $$x = \frac{13.094}{1.264}$$

$$= 10.37 \text{ mA}$$

At this beam current, the estimated absorbed dose during the irradiation can be calculated using the dosimetry data obtained earlier as described in Chapter 3.

Working flow rate (estimate) = 200 Nm^3/hr

Working volume of vessel = 0.127 m^3

Retention time t_r = $\frac{0.127}{200} \times 3600$ s

= 2.286 s

Estimated dose at 2 mA for 90 s exposure = 111.96 kGy *

Hence

Working estimated dose = $\left(\frac{2.286}{90} \times 111.96\right) \times (\frac{10}{2})$

= 14.21 kGy

(*Note: this value was obtained from the dosimetry exercise carried out earlier separately)

The absorbed dose value was slightly higher than the anticipated value of up to 10 kGy (IAEA-TECDOC-1189 (2000), IAEA-TECDOC-1023 (1998),) (Namba (1995), Basfar (2008)). The dominant pollutant in the diesel emission was nitric oxide. In the other systems, the fuel used was high sulphur coal where the main pollutant was sulphur dioxides. Removing SO_2 requires a lower dose between 5 – 8 kGy as mentioned by Licki (2002 and 2013). This study had proven that higher dose is needed to remove nitric oxide.

The electron beam parameters that were used to produce this dose were:

Beam energy	=	1 MeV
Beam current	=	10 mA
Beam power	=	10 kilowatts

Removal of nitric oxides by electron beam irradiation was achieved via oxidation process. When using electron beam, gas-phase radicals such as O. OH and HO_2 were generated by electron impact excitation and ionization. These radical would then react with the pollutants within the gas flow.

Electron beam irradiation technique used in the experiment was sufficient to remove up to 90% of NO in real diesel exhaust. However, to make the system more efficient it requires high power, with beam current > 10 mA. For commercial application, this may not be very economical. Therefore, the compromise would be to use beam current

ranging between 8 to 10 mA. For this test rig beam current of 10 mA to produce dose of 14 kGy, was proven to be the most effective.

The actual power requirement also depended on the efficiency of the electron beam machine itself as well as the overall system. For a Cockroft Walton type electron beam machine, such as the EPS 3000 used in these experiments, the efficiency is up to around 80% (Fairand 2001). Hence, the power required to produce the 10 kW was 12.5 kW, and there are no significant drops or losses that need to be included in the operational cost. However, for other types such as the ELV machines that are using transformer power supply, the efficiency is known to be much lower. This would require higher input power to achieve the same results making it more costly to operate.

The test rig used in the experiments was also optimized by providing favorable conditions inside the process vessel in terms of processing humidity and temperature. It was observed that increasing the humidity did not improve the removal rate of NO as initially expected. According to Chmielewski (2002) additional humidity or water molecules in the system, had a strong influence in the removal of SO_2 rather than NO/ NO_x. The oxidation-reduction cycle between NO_2 and NO had also made it difficult to increase the removal efficiency without increasing the dose or power consumption. Licki (2013) suggested that the optimum removal efficiency for the system was 11% v/v which is the humidity maintained in our test rig.

Other additives such as alcohol and ammonia had also been shown to improve the removal rates (Chmielewski 2002). In most experiments carried out at other installations, the purpose of adding ammonia was to capture or neutralize the acids formed during the irradiation inside the process vessel. In the presence of ammonia, heterogeneous reactions described earlier will dominate. The HNO_3 droplets formed by the reactions would react with the ammonia to form nitrate-based substance:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

This reaction is irreversible at temperature less than 150 °C and may influence the NO_x removal. Matzing (1992) had described the removal mechanism scheme of NO_x in the presence of ammonia as below:

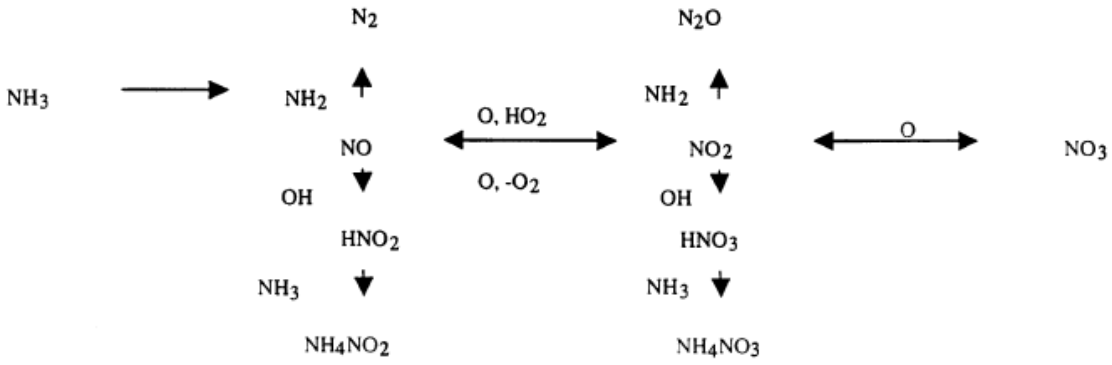


Figure 5.7: Removal mechanism of NO_x in the presence of ammonia.

The scheme shows that O atom and the OH, NH_2, HO_2 free radicals play important roles in the NO_x removal process. Organic compounds such as alcohol produce OH and HO_2 free radicals that can react with NO_x in a chain reaction process. Thus, adding alcohol into the EBFG system can further improve the efficiency. Several experiments had been carried out by Chmielewski (2002) to prove this idea although more intensive work are required to study its viability for industrial applications.

Another way to increase the efficiency and optimize the power consumption is by using multi-stage irradiation as suggested by Chmielewski et al. (1995) and Matzing (1996). It was proposed that the highest dose would be needed at the first stage and lower at the second, and eventually if applicable at the third irradiation stage. Multi-staged irradiation will not necessarily mean having to have several electron beam machines. The Budker Institute of Nuclear Physics had developed an accelerator with multiple accelerating tubes (Salimov (2000) and Auslender (2002)). Using this type of design would reduce the cost of high voltage source for the accelerator.

CHAPTER 6:

REMOVAL OF NITRIC OXIDES IN GASEOUS PHASE USING DIELECTRIC BARRIER DISCHARGE

This chapter presents all results from experiments that have been carried out using dielectric barrier discharge reactor to remove nitric oxide in gaseous phase. Unlike the EBFG experiments, the gases used in the experiments using the DBD were from bottled mixture of gases with known concentrations. The results will be presented chronologically, from the preliminary stage until the optimization stage. Various parameters were investigated to find the optimum configuration for the reactor.

6.1 Preliminary results

The main objective of the preliminary work was to find out whether the DBD reactor could be used for direct processing of contaminated air stream. Throughout the studies, the applied or input voltage is used as reference only. In the preliminary work, the original basic power supply with maximum voltage of 28.2 kV was used. Known concentrations of NO from a bottled source were also used. The initial concentration was 51.2 ppm while the balance was a mixture of SO_2 (30 ppm) and nitrogen. The flow rate was controlled by the flow meter on the DBD reactor. A chemiluminescence's type NO analyzer (TEI Corporation, model 42C) was used to analyze the output continuously throughout the process. The removal efficiency was calculated by using the same equation used for the EBFG:

$$\eta(\%) = \frac{[NO(in)] - [NO(out)]}{NO(in)} \times 100$$

When investigating the effect of variable discharge voltages, the flow rate was fixed at 1 scfh (standard cubic foot per hour) to control the consumption of the NO gas. The effective gas volume treated, i.e. the volume of gas that actually in contact with the plasma, was calculated to be approximately 0.05 liter (details in Chapter 3). The retention time, i.e. the amount of time the gas in contact with the micro discharges was calculated to be 7.63 seconds. The discharge voltage was later fixed at 28.2 kV (the maximum output voltage available at this stage) when running the experiments at different flow rates.

Figures 6.1 and 6.2 show the effect of varying discharge voltages on the removal efficiency for two DBD tubes connected in parallel and in series respectively. Both figures show that the concentration of nitric oxide was reduced with increasing voltage.

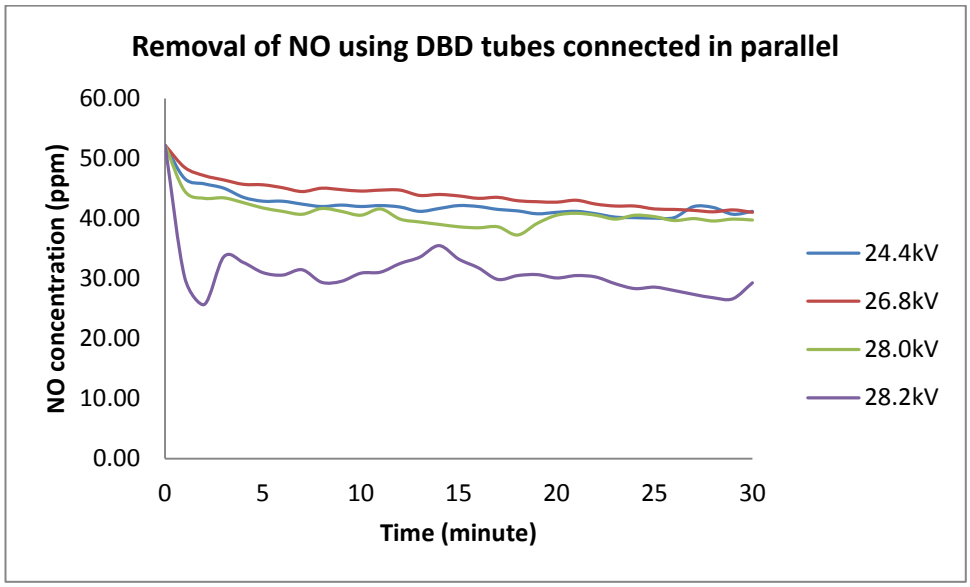


Figure 6.1: Removal of NO with 2 DBD tubes connected in parallel.

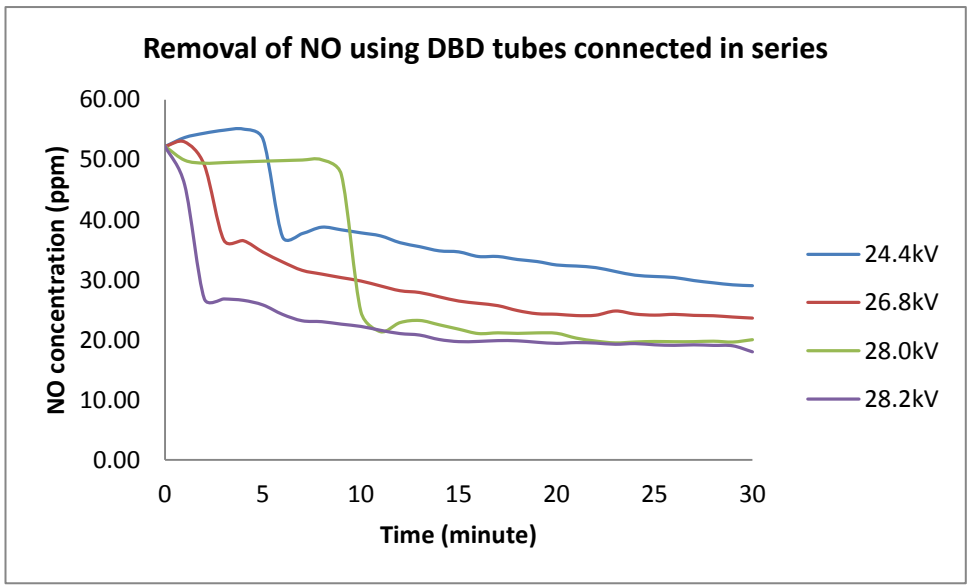


Figure 6.2.: Removal of NO with 2 DBD tubes connected in series.

The removal efficiency was found to be improved by connecting the two tubes in series instead of parallel. The maximum efficiency for the case of parallel connection was 49% and it was increased to 63% for serial connection. The improvement was significant and the serial connection will be adopted for future work. By connecting the tubes in series, the total processing rate was reduced compared to parallel connection. This became a factor that needed to be further investigated. In the application of electron beam for flue gas treatment, double or multi-stage irradiation had been proven to be more effective than single stage irradiation (Chmielewski 1995).

Figure 6.3 shows the side by side comparison between the two types of connections at different voltages. The chart also confirmed that the removal rates were higher for both conditions at higher voltage.

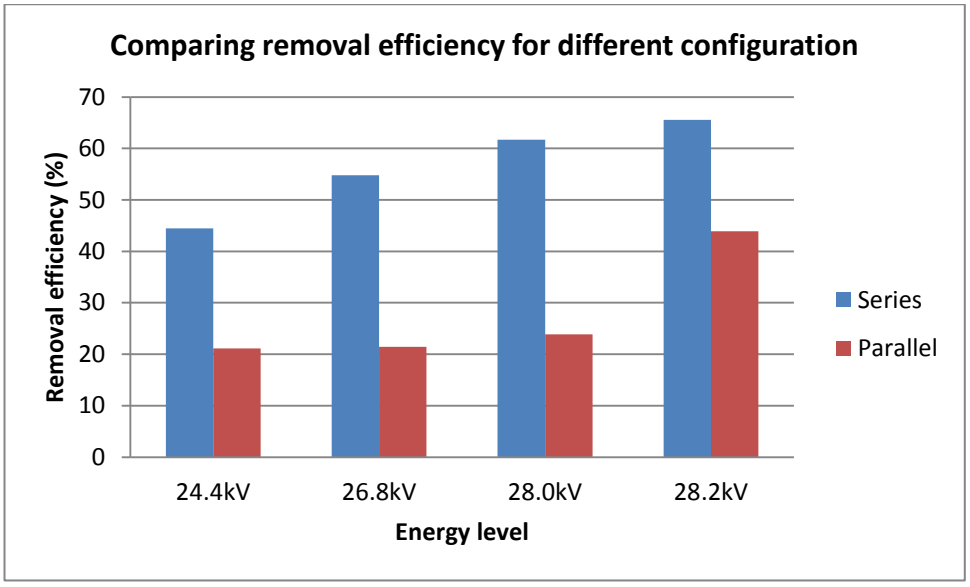


Figure 6.3.: Side by side comparison of efficiencies for serial and parallel connections.

Varying the flow rate will affect the retention time of the targeted pollutant inside the DBD tube. In theory, higher flow rate (thus shorter retention time) will result in lower removal efficiency. Figure 6.4 shows result of experiments carried out by varying the flow rate at fixed voltage. There were no significant changes recorded on the concentration of NO in this case. This could be due to the insufficient energy to induce more chemical reactions inside the tubes. This is another area that was investigated further in the later part of the experiments.

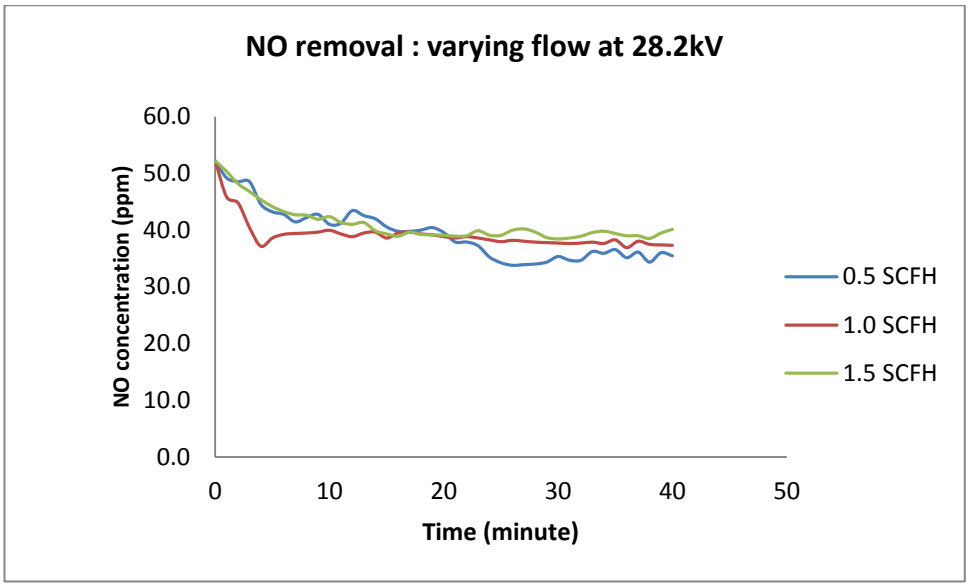


Figure 6.4: Removal of NO at different flow rates and fixed energy.

At this point, it was possible to assume that some nitric oxide was reduced to nitrogen gas since oxygen was absent in the gas mixture. However, since SO_2 was also present and some reaction may cause O_2 to be separated and reacted with the NO to produce NO_2 by oxidation.

The following conclusions were derived from the preliminary results:

a. Higher voltage (more than 28 kV) was needed for better efficiency
b. Serial connection gave better results than parallel connection
c. The efficiency may be affected by the flow rate.

These conclusions were very useful to set the parameters for the next phase of experiments. Better power supply was used as described in Chapter 4. Further investigations were also planned to study the effect of background gases, flow rate and various tube configurations.

6.2 Effect of Background Gases (Phase 2 experiments)

Having determined the basic requirement to achieve good removal rate, the reactor was upgraded by using a power supply that can provide up to 35 kV voltage to the tubes. The tubes were clean and connected in series throughout the experiments.

The experimental conditions were based on the gas composition as stated below

Condition A. Nitric Oxide (100 ppm) and nitrogen only (as balance gas)

Condition B. Nitric Oxide (100 ppm) + Sulfur dioxide (300 ppm) and nitrogen gas (as balance)

Condition C. Nitric Oxide (100 ppm) + Sulfur dioxide (300 ppm) + nitrogen gas (as balance) and added atmospheric air.

Figure 6.6 shows a typical result when using the DBD to remove NO in gas stream with only nitrogen gas as background (Condition A). In this case, the gas was flowing at 4 standard cubic feet per hour (scfh), using 2 DBD tubes in series. The peak to peak voltage was set at 32 kV. Oxidation had occurred in the first 2 minutes where the amount of NO_2 was observed to have peaked. Eventually the NO_2 had subsided in time where almost complete removal was achieved. This is an ideal situation where NO remediation was totally achieved by the reduction pathway. This proved that reduction can be achieved with sufficiently high energy.

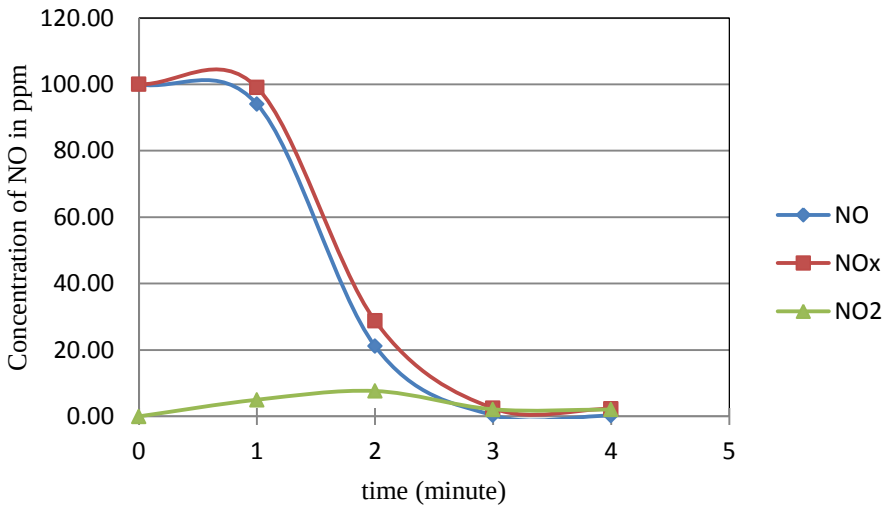


Figure 6.6: Removal of NO from gas stream with N_2 as background using 2 DBD tubes at 32 kV and flow rate of 2 scfh.

When a gas mixture containing SO, NO and N_2 was used, the oxidation process had occurred as shown in Figure 6.7. The concentration of NO_2 resulted from the oxidation was very low. This result was obtained when 2 tubes are connected in series and the voltage was set at 32 kV and with gas flow rate of 2 scfh. The efficiency of this set up was investigated further by increasing the flow rate up to 5 scfh. As expected, the

removal rate dropped from 92% to 70% when the flow rate was increased from 2 scfh to 5 scfh. The other results are shown in Table 6.1.

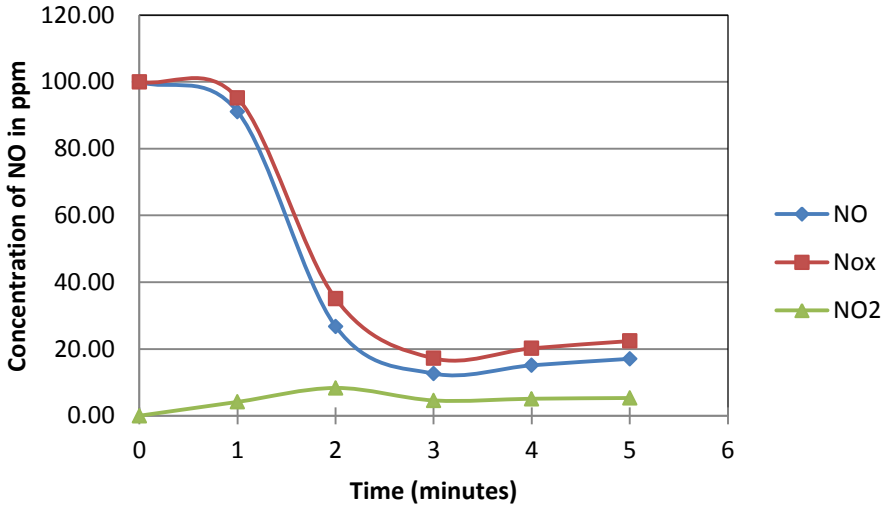


Figure 6.7: Removal of NO from gas stream containing NO, SO_2 and N_2, using 2 DBD tubes at 32kV and flow rate of 2scfh

Table 6.1 Removal rate of NO from gas stream containing NO, SO_2 and N_2, for different flow rate using 2 DBD tubes in series and at voltage of 32 kV.

Flow rate (scfh)	**Removal rate (%)**
1	(40.51)
2	91.95
3	89.83
4	82.95
5	69.93

In another series of experiments, atmospheric air was injected separately into the system at a steady flow of 0.5 scfh in addition to the gas. The air contained moisture which eventually caused results to be rather erratic as seen in Figure 6.8. Oxidation was the dominant process and the energy of the discharges from the two tubes were insufficient to promote the reduction pathway. The final removal rate was approximate 40% and since the final product contained significant amount of NO_2, post treatment may be necessary. This situation was similar to that using the EB irradiation.

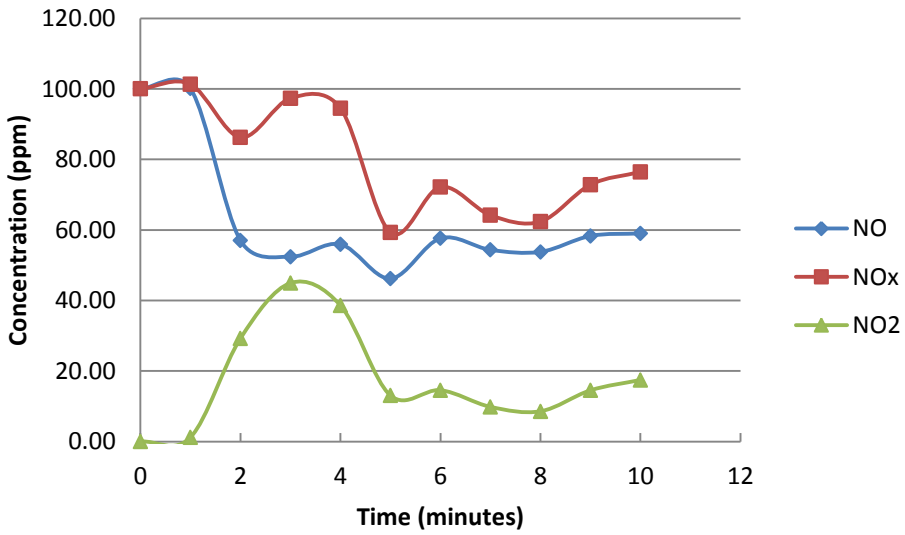


Figure 6.8: Removal of NO from gas stream containing NO, SO_2 and N_2 with added air, using 2 DBD tubes in series at voltage of 32 kV and flow rate of 2 scfh.

The experimental results show that oxidation will occur in all gas conditions especially when moist air is present (gas condition C). In situation A and B where the air was limited, the reduction pathway became dominant after about 2 minutes of processing. Experimental results also show that the inlet gas composition has some effects on the removal rates of NO. Nitrogen gas, being inert, did not have any significant effect to the removal of NO in all cases. Additional SO_2 did affect the removal to a certain degree

with variation of flow rate. Air on the other hand, has greater effect since it provided additional oxygen and possibly water molecules to enhance oxidation process. The results gave some basis for further investigation on how to optimize the DBD reactor for NO remediation.

6.3 Effect of Flow Rates

In the previous preliminary experiments (Hashim et. al. 2007) it was found that the removal rate was also affected by increasing the flow rate. However, in this experiment, using condition A, the effect was not significant until it reached more than 10 scfh (Table 6.2). Higher flow rate reduced the retention time and thus reducing the probability of interaction between the energized electrons and the gas molecules to induce chemical reactions.

Table 6.2. Removal rate of NO from gas stream with N_2 as background, at different flow rate.

Flow rate (scfh)	Removal rate (%)
1	99.99
2	99.84
3	99.04
4	99.99
5	99.99
10	72.64
15	30.36

6.4 Effect of Number of Tubes

Table 6.3 gives the summary from another series of experiments using condition A, but this time the number of DBD tubes used was varied. In all cases, except when using 4 tubes, the removal rate was 99%. When using more than 3 tubes, the discharge current on each tube was reduced and become insufficient to react with the gases. Although the tubes were connected in series, the electrical connection was in parallel. In this situation, the voltages across the tubes were equal but the current was divided by the number of tubes. Therefore it was necessary to determine the number of tubes that can give the optimum results.

Table 6.3. Removal rate of NO from gas stream with N_2 as background, using different number of DBD tubes.

Number of tubes	Removal rate (%)
1	99.9
2	99.6
3	99.5
4	93.4

The experiment was repeated using gases in **condition B** for different number of tubes at fixed flow rate of 2 scfh. The summary of the results is as presented in Figure 6.9. It shows that the efficiency increases with the number of tube in a polynomial manner and saturates at around 90%. The results show that to achieve 90% efficiency, 7 tubes are sufficient.

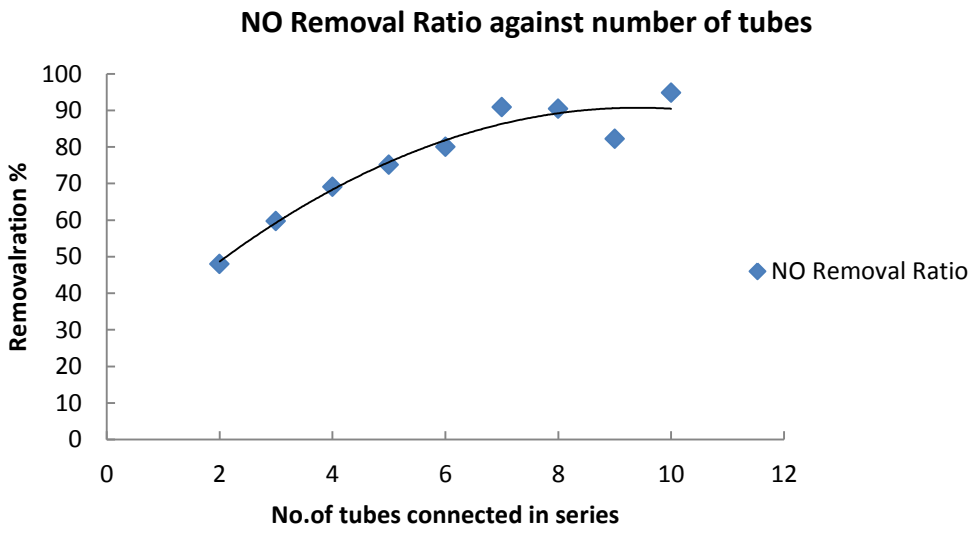


Figure 6.9 Relationship between the removal efficiency and the number of tubes connected in series. Experiments were carried out using mixed gas at Condition B.

6.5 Optimization of the DBD reactor (Phase 3 experiments)

The basic factors or issues that have been identified to have effects on the efficiency of the reactors were the flow rates and background gases. These issues may be overcome by improving the input power, number of tubes used and the configuration of the tubes. With the limited number of useable tubes, we need to find out the optimum configuration to deploy a viable reactor to remove nitric oxide in mixed gases.

Although the actual diesel emission could not be implemented in this reactor, the gas mix in Condition B would give general ideas on the behavior of the plasma chemical process in flue gas environment in the reactor. Based on the results obtained in this project, total elimination of NO is possible for cases where the background gas is

nitrogen. However, with mixed gases, this may not be possible since other compound will also contribute to the oxidation pathway. To match the EBFG efficiency, the removal efficiency of the reactor has to be between 47 to 90% (refer to Figure 4.6). However, for the purpose of finding the optimum parameters for the reactor and based on the available results, 30% removal efficiency was set as the minimum target and 80% removal efficiency the optimum target. This should give a good indication on the reactor's capabilities.

6.5.1 Optimum voltage

Our results indicated that voltage between 30 to 35 kV had produced the highest efficiency. As described earlier, although the tubes were connected in series, the electrical connection was still in parallel. This means that each tube have the same applied voltage. However, the current will be divided by the number of tubes. Hence there is an optimum number of tubes that can be supported by a power supply with a fixed output power capability. Another limiting factor for the optimum voltage is the maximum voltage that each of the DBD can stand without reaching the breakdown point. When there is a complete gaseous discharge (probably a glow discharge if the current is controlled within the mA range) the energetic electron streamer (the filamentary discharge) will disappear and the desired chemical reaction will not take place. In this case, the limitation of the 35 kV is believed to be caused by the limitation of the current that can be supplied by the power supply. If the voltage has exceeded the discharge breakdown voltage of the DBD tube the NO removal efficiency will drop drastically.

6.5.2 Investigation on the effect of DBD tubes arrangement

It was established earlier that serial configuration gave the better efficiency but the processing flow rate was lower compared to the case of parallel connection. In the final phase of experiments, combinations of tubes configuration or arrangement were tested at fixed input voltage of 32 kV, using gas condition B. The flow rate was varied between 1 scfh to 11 scfh.

Figures 6.10 to 6.13 are results for tubes connected in the (Xs//Xs) combinations, where X = 2, 3, 4 or 5. In each graph, the corresponding flow rate that achieved 30% and 80% removal rates were noted. The summary of the values are tabulated in Table 6.4. For example, in Figure 6.10, when 2 sets of two tubes in series, connected in parallel, the corresponding flow rate that achieved 30% and 80% removal were 5 scfh and 2 scfh respectively.

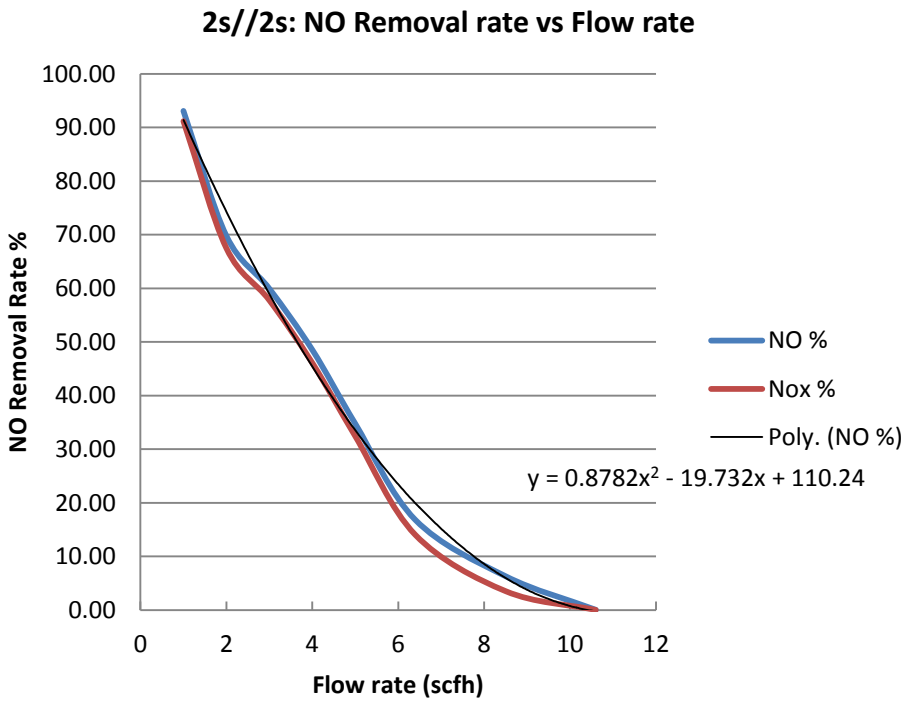


Figure 6.10 : NO Removal rate vs Flow rate for 2s//2s configuration.

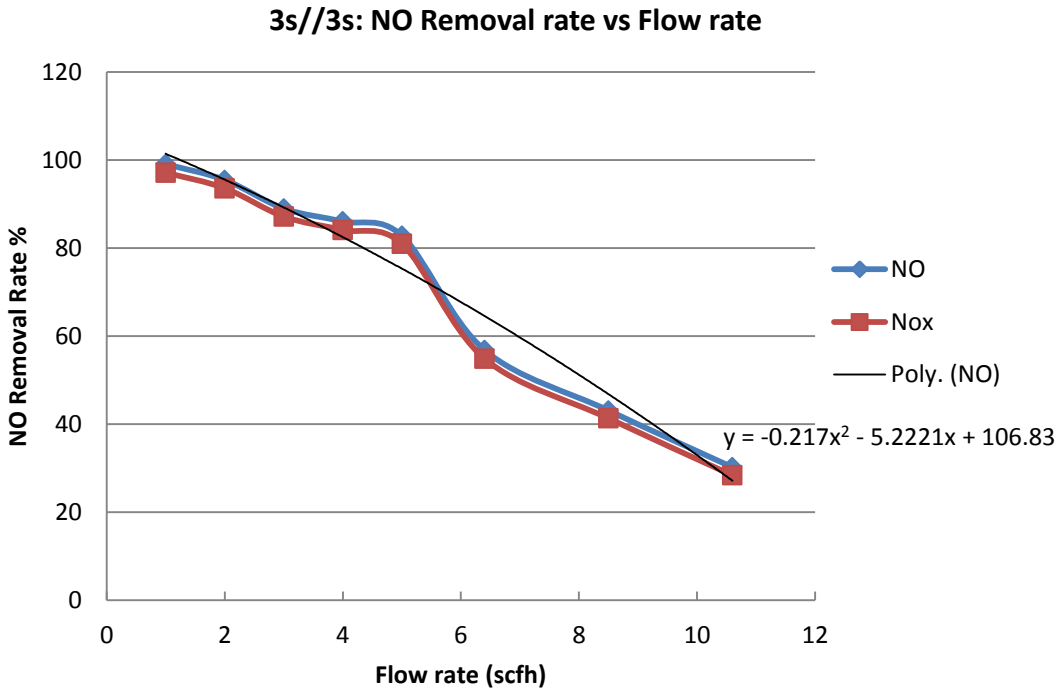


Figure 6.11: NO Removal rate vs Flow rate for 3s//3s configuration.

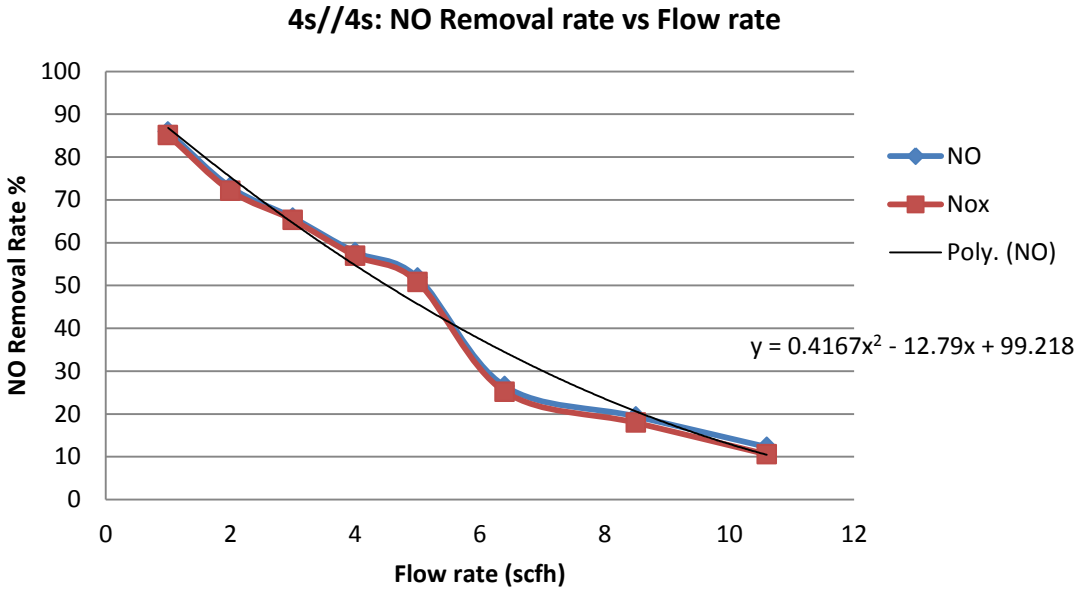


Figure 6.12: NO Removal rate vs Flow rate for 4s//4s configuration.

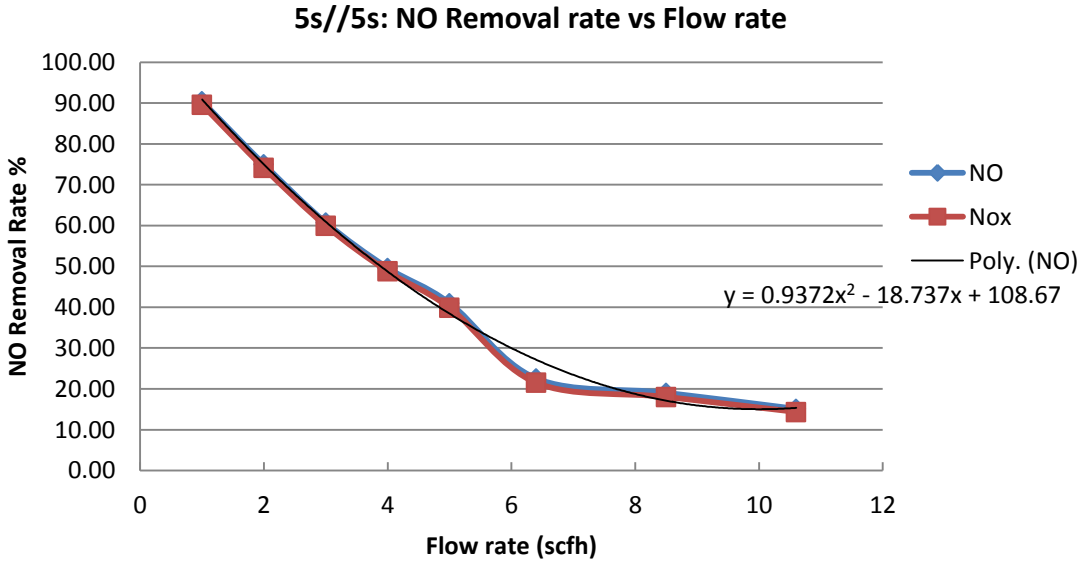


Figure 6.13: NO Removal rate vs Flow rate for 5s//5s configuration.

Table 6.4. Summary of results for 30% and 80% removal efficiency.

Configuration	Flow rate to achieve 30% removal (scfh)	Flow rate to achieve 80% removal (scfh)
2s//2s	5	2
3s//3s	10	5
4s//4s	6	1.8
5s//5s	5.5	2

The results in Table 6.4 did not show a linear relationship between the tube configuration and flow rate. It shows that the best results were achieved when using two sets of 3 tubes in series connected in parallel, which gives the total of 6 tubes used. The 4s//4s and 5s//5s configurations resulted in lower flow rate to achieve the targeted efficiency. In this case the total numbers of tubes used were 8 and 10 respectively.

Figures 6.14 to 6.16 are results for tubes connected in the N(2s//2s) combinations, where N = 3, 4 or 5, which is the number of sets of 2s//2s to be connected in parallel. The 2s//2s was chosen to be the basic configuration for easy handling. Figure 6.14 for example was the result when 3 sets of 2 tubes in series (total of 6 tubes), connected in parallel. The graph shows decrease in the removal efficiency as the flow rate was increased. The trend was the same for the 4(2s//2s) configuration (total of 8 tubes). The 5(2s//2s) configuration (total of 10tubes) however, did not give significant results as the

removal efficiencies for all flow rates were low (below 30%). Again, this shows that the total number of tubes have significant effect on the removal rate. It was established earlier that 7 tubes were optimum and in these two cases, six and eight tubes gave the most significant results.

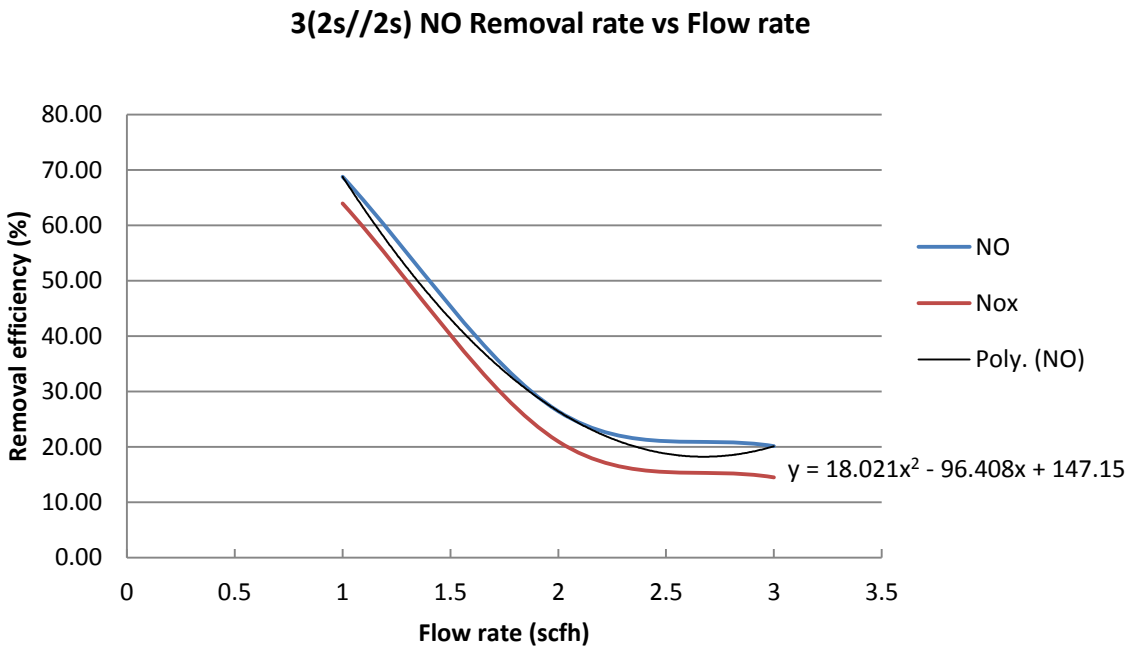


Figure 6.14: NO Removal rate vs Flow rate for 3(2s//2s) configuration.

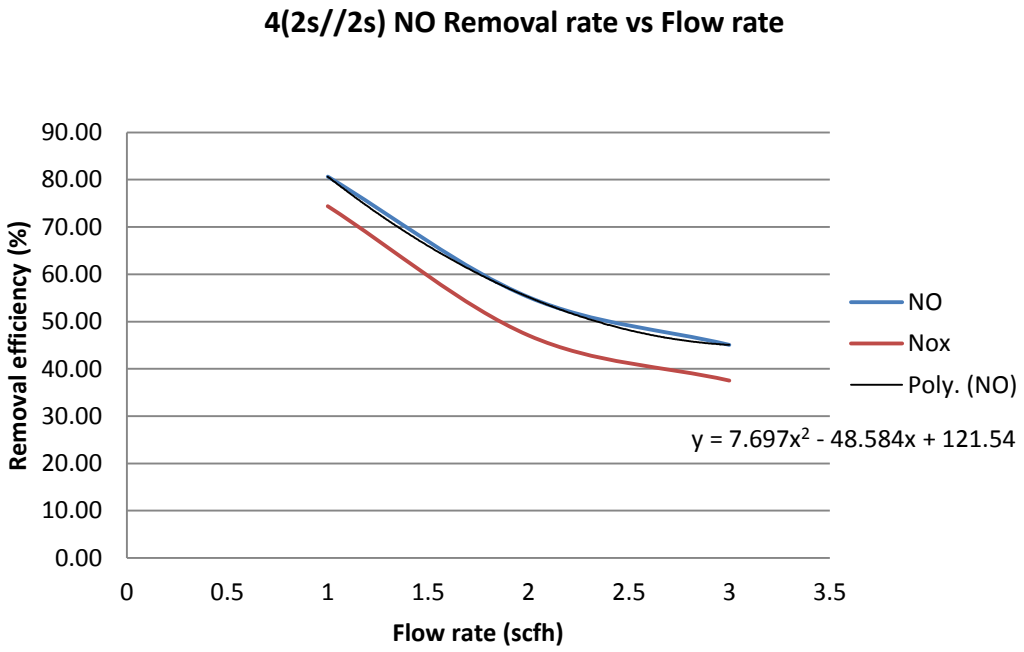


Figure 6.15: NO Removal rate vs Flow rate for 3(2s//2s) configuration.

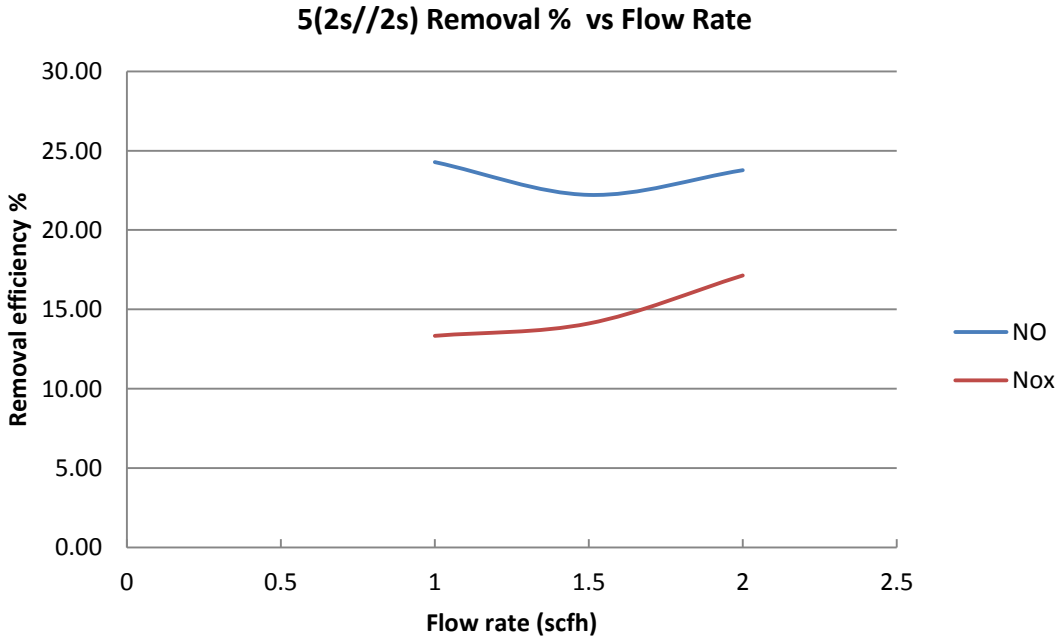


Figure 6.16: NO Removal rate vs Flow rate for 5(2s//2s) configuration.

From the above experiments, it was shown that the (3s//3s) arrangement was the most suitable tube configuration for a practical DBD based reactor operated with a voltage between 30 - 35 kV. In this arrangement, 6 tubes were used which in agreement with the maximum of 7 as earlier concluded. With this configuration, it was demonstrated to be able to process mixed gases at the rate of 5 scfh with 80% removal efficiency (Figure 6.11 and Table 6.4). Although processing lower flow rate (1scfh) can produce almost 100% removal, the economic aspects must also be taken into account. However, the decision on which configuration or arrangement to adapt will depend on the application. If higher flow rate processing is required, then some modifications should be made especially on the power supply that can provide sufficiently high energy to promote reduction.

CHAPTER 7

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

In this study two concepts of remediation of nitric oxides in gaseous form were evaluated experimentally. The main principle behind the experimental setups was plasma oxidation in gas phase. The experiments were carried out using two different methods of producing electron beam based on electrical discharge. The common factor in the two methods is the energetic electrons. In the EBFG system, electrons gain energy as they pass through high voltage gradient in vacuum tube. The electrons are in the form of a continuous beam that travels with energy up to 3 MeV. In the experiments conducted, the energy was limited to 1 MeV for economic reasons. In the dielectric barrier discharge, on the other hand, the electrons are produced in short pulses. The electrons are expected to have a spread of energy limited by the input discharge voltage.

This chapter will draw conclusions from the experiments carried out using both methods. Comparisons are also made between the two methods. Suggestions for future work are made based on the potentials of each method and will set the directions for future work.

7.1 CONCLUSIONS

Investigations using the electron beam for flue gas treatment indicate that processing temperature, moisture content, beam current and radiation dose are the important parameters in determining the removal efficiency of nitric oxides. Removal efficiency of at least 90% was obtained by keeping the humidity of the flue gases at the inlet, to about 13% v/v and temperature around 70 °C. The absorbed radiation dose was estimated to be around 14 kGy. The radiation dose is linear to the value of beam current and for this test rig 10 mA is sufficient to obtain the desired results. Although higher beam current will give better results, it will also mean added cost for energy consumption.

Experiments using the DBD reactor were carried out at room temperature using different mixtures of gases. Results obtained using only NO in N_2 background showed that removal of NO was achieved by the reduction of NO and reaction with N to form N_2 and O. Removal efficiency of higher than 90% was easily achieved. In the presence of other gases such as SO_2 and O_2, the oxidation process was more prominent where acids will be formed and additional post treatment will be needed to neutralize it. This was overcome by providing more electrical discharges by mean of increasing the input voltage and adding the number of DBD tubes in the reactor. In the end, a reactor using 6 tubes configured to have 2 sets of 3 tubes in series connected in parallel (coded as 3s//3s) had been tested to be effective for NO removal. When operated with 35 kV as the input voltage, the reactor can remove up to 80% nitric oxide in the reduction mode. This means that the energy is sufficiently high to sustain the reduction mode and prevent further oxidation. Hence, additional treatment is not needed at the outlet point.

Direct comparisons between the two methods are not justified due to the vast difference in the scale of experiments. The EBFG is capable of treating up to 10,000 NM^3 of flue gases whilst the DBD can treat at the highest, 0.28 m^3/hr (10 scfh) using 7 cells. In order for the DBD to match the processing rate of the EBFG, it will need 250,000 cells. This will require extremely large space to install and will not be practical. However, the DBD based reactor can be ideal as a portable device for small to medium scale treatment. This will be discussed in the suggestion for future work section.

However, there are some aspects where comparisons can be made. First of all, in term of safety, both technologies demands strict electrical safety since the processing involves high voltage. As a table top reactor, the DBD can be classified as a normal consumer electrical product as long as it passes the electrical safety test. The main voltage to the EB machine, on the other hand, comes from its own 11 kV substation that must comply to the TNB's standards. It has its own transformers, power reactor and inverter to provide input voltage to the Cockroft Walton voltage multiplier circuits. This equipment must be installed in a separate and secured room. The same requirement may be applied for the DBD reactor if it is required to be scaled up.

The EB machine produces accelerated electrons which are also known as beta radiation. All radiation sources must come with sufficient radiation shielding. Although beta radiation has limited penetration power, the radiation shielding requirement is still very high. The reason is that when electron in the MeV energy bombards at material, especially metallic material, it will produce X-ray radiation by the bremsstrahlung

effect. The radiations produced are high energy X-rays that have much greater penetrating power. Hence the shielding is calculated based on the penetration of the X-ray. The EB machine located at Nuclear Malaysia has maximum energy of 3 MeV. The overall shielding thickness required is 2.5 m of high density concrete. This special requirement will add to the construction cost. In addition, radiation monitoring is also mandatory as part of the plant's radiation protection plan. This requirement is as stated in the Act 304 (Atomic energy Act 1994). The DBD reactor on the other hand has negligibly low radiation hazard.

The DBD reactor is modular which means that it can be scaled up easily. This means that the reactor can be designed to process low to high flow rate of gases, depending on the specific need, simply by adding or reducing the number of DBD tubes. The right balance between the input high voltage and the flow rate will determine its cost effectiveness.

The EB flue gas treatment needs pre-determined processing parameters such as the flow rate, flue gas conditioning, accelerator voltage and beam current before the system can be constructed. The number of electron beam accelerators needed will be determined by the flow rate since multiple stage irradiations is preferred. It is also important to design a backup plan in case an accelerator breaks down. Hence at least two electron beam machines are necessary to ensure continuous processing. At present, electron beam machines are reliable industrial tool provided proper maintenance is observed.

Capital cost will be an important determining factor to set up an environmental remediation facility in any industrial or commercial plants or factories. Such set up are normally seen as something that does not bring tangible benefit to the organization unless it is made mandatory. At the same time, the technology must be proven viable to attract users. The electron beam flue gas treatment is a proven technology that has been demonstrated by industrial installation. One example is the installation of the system at Pomorzany Power Station in Poland. (Basfar 2010, Chmielewski 2003). The treatment plant consist of two 1 MeV EB machines to treat 100,000 Nm^3/hr of flue gases. The main attraction of this system is that it is capable of treating NO_x and SO_2 simultaneously and producing byproducts that can be turned into fertilizers. The power plant is fuelled by coal which is known to have contributed to air pollution in Europe since the age of industrial revolution.

It should be noted also that currently, electron beam machine installed in Malaysia are all imported since the technology has not been mastered by the local industry. This alone will set high price on the machine. The DBD technology however is homegrown and the manufacturing is more cost effective. The simple rule in manufacturing where the cost will be lowered by the number of duplicates made, is applicable. Since a large scale DBD reactor is expected to consist of a large number of tubes, it is anticipated that a breakdown in a single tube will not disrupt the processing. This will not be possible for EBFGT system since its processing rate is dependent on the electron beam machine itself. Even if the installation comprises 2 or more EB machine, it will still be required to reduce the total processing rate or in worst case, complete halt until the machine is back in operation. Hence regimented maintenance plan must be adhered strictly to ensure continuous treatment process.

7.2 SUGGESTIONS FOR FUTURE WORK

In both EBFG and the DBD methods, the targeted pollutant was nitric oxide which is the main component in gases produced from diesel combustion. However, there are other components which are harmful to the environment such as volatile organic compounds (VOC) and poly aromatic hydrocarbons. These compounds are potent atmospheric pollutants that are also required to be addressed. This extension will require more complex analysis systems such as FTIR or other spectroscopy equipment (Ostapczuk 2008).

The work using DBD should be extended to test actual emission from diesel combustor. This will give a better outlook of its potential. One of the potential is to test it to treat emission from diesel-run vehicle such as cars, lorries and even ships. The results from this work are insufficient to conclude its suitability for direct applications in car exhaust. The main issue is the flow rate.

Since the results of this study shows that the current DBD design is suitable for low flow rate treatment, another potential use is to treat gaseous emission in kitchens that uses natural gas for cooking. Natural gases as stated earlier in the introduction emits NO and NO_x. Although there are no regulations to control household air quality, it would be a good practice for the sake of health, to remove anything that may pose threat to the occupants.

The EBFG test rig installed at Nuclear Malaysia can be used to do further work on treatment of diesel emission since most advance work have been focused on coal-fired pollutants. One potential industry that may use this technology is in commercial shipping. NO_x emissions from marine diesel engines are of concern to the international community because of its toxic nature. (Burgel 2007). This has been recognized by the International Marine Organization (IMO), in which Malaysia is a member state. IMO ship pollution rules are contained in the "International Convention on the Prevention of Pollution from Ships", known as MARPOL 73/78. On 27 September 1997, the MARPOL Convention has been amended by the "1997 Protocol", which includes Annex VI titled "Regulations for the Prevention of Air Pollution from Ships". MARPOL Annex VI sets limits on NO_x and SOx emissions from ship exhausts, and prohibits deliberate emissions of ozone depleting substances. The latest amendments to the Annex VI was adopted in October 2008 where new fuel quality requirements were introduced and entered into force beginning from July 2010. It also introduced Tier II and III NO_x emission standards for new engines, and Tier I NO_x requirements for existing pre-2000 engines.

With these new enforcement requirements, new technologies are also needed to realize the target of cleaner air even in the sea. This opens a new opportunity for new research using the two plasma-discharge methods presented in this study to treat the emission from ships.

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AWARDS

1. **Silver Medal Award** at the International Exposition of Research and Inventions of Institutions of Higher Learning 2009
   Title of Project: Discharge Based Reactor for Chemical Syntheses

2. **Gold Medal Award** at the Research, Invention & Innovation Expo University of Malaya 2006. University of Malaya. 2006
   Title of Project: Discharge Based Reactor for Chemical Syntheses

3. **Research Grant** from the Institute of Research Management and Consultancy (IPPP), Universiti Malaya to value of RM 16000.00
   (IPPP/UPDit/Geran(RU/PPP)/PS070/2007C, December 2007)

4. **Research Grant** from the Institute of Research Management and Consultancy (IPPP), Universiti Malaya to value of RM 2384.00
   (IPPP/UPDit/Geran/P0169/2006A/2006A, August 2006)

APPENDIX A

Current NO_x control technologies. This table can be used to screen the potential technology to control NO_x.

Technique	Description	Advantages	Disadvantages	Impacts to consider	Applicability	NO_x reduction
LEA (Low access air)	Reduces oxygen availability	Easy operational modification	Low NO_x reduction potential	High CO emissions, flame length, flame stability	All fuels	1 - 15%
OSC (Off-stoichiometric combustion):a.BOOS (Burners out of service) b. OFA (over-fire air) c. Air lances	Staged combustion, creating fuel-rich and fuel-lean zones	Low operating cost, no capital requirement required for BOOS	a. Typically requires higher air flow to control CO; b. relatively high capital cost; c. moderate capital cost	Flame length, forced draft fan capacity, burner header pressure	All fuels; multiple burner devices	30 - 60%

Technique	Description	Advantages	Disadvantages	Impacts to consider	Applicability	NO_x reduction
LNB (Low NO_X burner)	Provides internal staged combustion, thus reducing peak flame temperature and oxygen availability	Low operating cost, compatible with FGR as a combination technology to maximize NO_x reduction	Moderately high capital cost; applicability depends on combustion device and fuel, design characteristics and waste stream.	Forced-draft fan capacity, flame length, design compatibility, turndown flame stability	All fuels	30 - 50
FGR (Flue gas recirculation)	Up to 20 - 30% of the flue gas recirculated and mixed with the combustion air, thus decreasing peak flame temperatures	High NO_x reduction potential for natural gas and low nitrogen fuels	Moderately high capital cost; moderately high operating cost affects heat transfer and system pressures	Forced-draft fan capacity, furnace pressure, burner pressure drop, turndown flame stability	Gas fuels and low nitrogen fuels	40 - 80%
W/SI	Injection of steam or water at the burner, which decreases flame temperature	Moderate capital cost, NO_x reductions similar to FGR	Efficiency penalty due to additional water vapor loss and fan power requirements for increased mass flow	Flame stability, efficiency penalty	Gas fuels and low nitrogen fuels	40 - 70%
RAPH (Reduced air Preheat)	Air preheater modification to reduce preheat, thereby	High NO_x reduction potential	Significant efficiency loss (1% per 40 F)	Forced-draft fan capacity, efficiency penalty	Gas fuels and low nitrogen fuels	25 - 65%

Technique	Description	Advantages	Disadvantages	Impacts to consider	Applicability	NO_x reduction
	reducing flame temperature					
SCRI (selective catalytic reduction)	Catalysts located in flue gas stream (usually upstream of air heater) promotes reaction of ammonia with NO_x	High NO_x removal	Very high capital cost, high operating cost, extensive ductwork to and from the reactor required; large volume reactor must be sited, increased pressure drop may require induced-draft fan, reduced efficiency, ammonium sulfate removal equipment for air heater required, water treatment of air heater wash required.	Space requirements, ammonia slips, hazardous waste disposal	Gas fuels and low sulfur liquid and solid fuels	70 - 90 %

Technique	Description	Advantages	Disadvantages	Impacts to consider	Applicability	NO_x reduction
SNCR (Selective non-catalytic reduction) - urea injection	Injection of urea into furnace to react with NO_x to form nitrogen and water	Low capital cost, relatively simple system, moderate NO_x removal, non-toxic chemical, typically low energy injection sufficient	Temperature dependent, design must consider boiler operating conditions and design, NO_x reduction may decrease at lower loads	Furnace geometry and residence time, temperature profile	All fuels	25 - 50%
SNCR (Selective non-catalytic reduction) - ammonia injection	Injection of ammonia into furnace to react with NO_x to form nitrogen	Low operating cost, moderate NO_x removal	Moderately high, capital cost; ammonia handling storage vaporization	Furnace geometry and residence time, temperature profile	All fuels	25 - 50%
*Electron beam flue gas treatment	High energy electrons are used to form radicals to react with the NO_x.	Simultaneous removal of NO_x and SO2. By products (ammonium nitrate and ammonium sulfate) can be used as fertilizers	High capital cost. Requires high electricity /power Removal of NO_x requires high power	Need more than 2 EB machine to ensure continuous process	Coal	High (more than 50%)

Source: DHF Liu 5.19 Gaseous Emission Control. In DHF Liu, BG Liptak (eds). Environmental Engineers Handbook, 2nd Ed. Boca Taton, FL: Lewis Publishers, 1997; Charles E. Baukal, Jr., Industrial Combustion Pollution and Control, Mrcel Dekker Inc. 2004 ;*Chmielewski

APPENDIX B

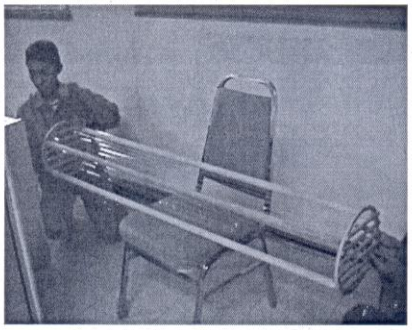
Scanned copy of dose mapping report from the Secondary Standard Dosimetry Laboratory, Malaysian Nuclear Agency.

Lapuran Pemetaan Dos : Vesel Penyinaran (Flue Gas) MINT

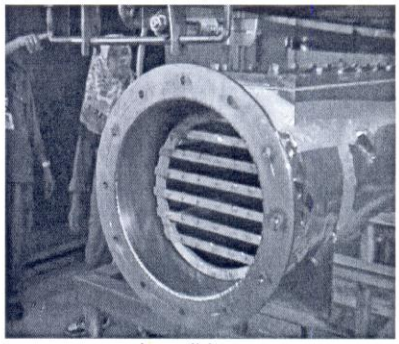
Tarikh pengukuran : 4hb. Oktober 2000

(1) Penyinaran : 1 MeV, 2mA dan 90 saat

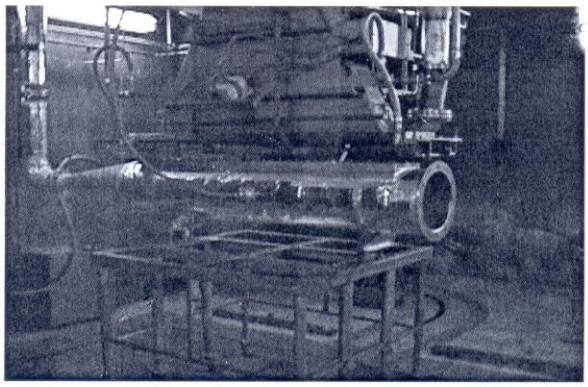
1.1 Kaedah penyusunan filem



(a)



(b)



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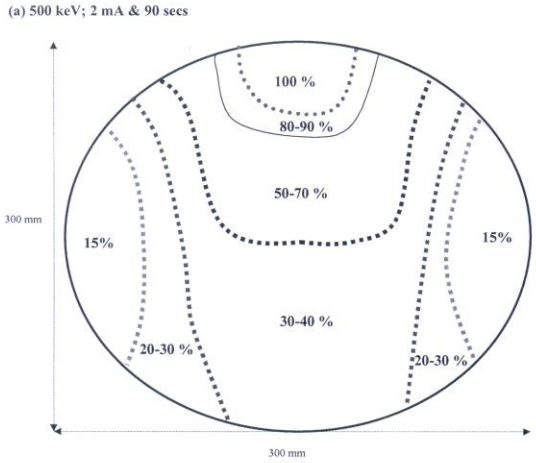
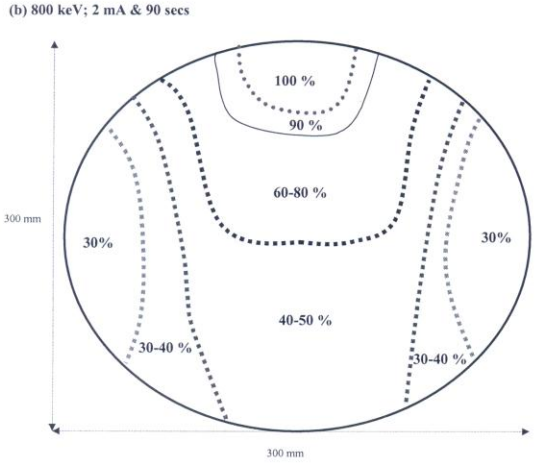
Rajah 1. Set-up penyinaran (a) penyusunan meterdos CTA pada panel kayu, (b) menempatkan panel kayu di dalam vesel dan (c) kedudukan vesel dalam bilik penyinaran.

1

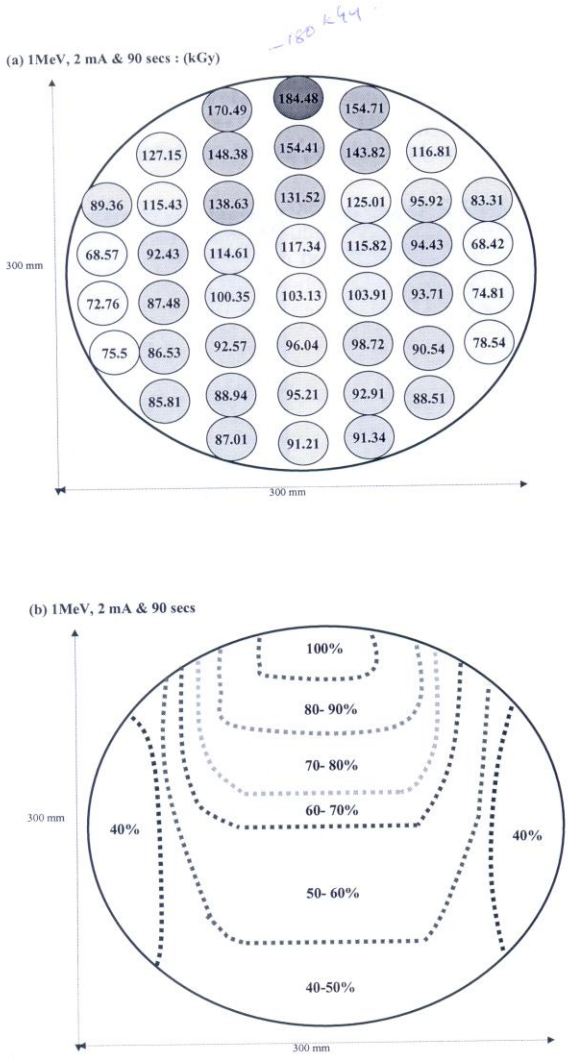
(2) Perbandingan taburan dos dengan tenaga-tenaga lain





Rajah 3: Penyinaran (a) 500 keV dan (b) 800 keV masing-masing pada 2mA dan selama 90 saat

1.2 Taburan Dos



Rajah 2: Penyinaran: 1 MeV, 2mA dan 90 saat

(3) Kesimpulan:

3.1 Penyinaran dengan tenaga 1MeV memberikan nilai keseragaman dos yang baik di dalam vesel penyinaran (Rujuk Rajah 2 dan 3).

3.2 Nilai kadar dos purata bagi penyinaran statik bagi 1 Mev, 2 mA dan 90 saat ialah 111.96 ± 28.97 kGy. Ianya dapat digunakan sebagai panduan untuk menauliahkan proses penyinaran (dari segi pemberian dos).

3.3 Kadar dos yang diterima oleh *flue gas* dengan kelajuan tertentu dapat ditentukan dengan meghubungkan nilai kadar dos di atas dan juga geometri vesel penyinaran berkenaan. Contoh: *flue gas* dengan kelajuan 400 Nm^3 sejam akan menerima dos sebesar 1.2 kGy semasa melalui vesel penyinaran (sekiranya disinarkan dengan parameter di atas).

3.4 Nilai ini dapat digunakan untuk menentukan parameter penyinaran sebenar bagi memperolehi kadar penyahan SO_2 dan NO_x yang berkesan dalam *flue g*as berkenaan.

Disediakan : Dr. Noriah Mod Ali
QA-SSDL

residence time = 1 sec.
at 400 Nm^3

plug flow

(6-8 kGy.)

=)

Blower power
→ losses on 1st & 2nd winding
& energy in PV